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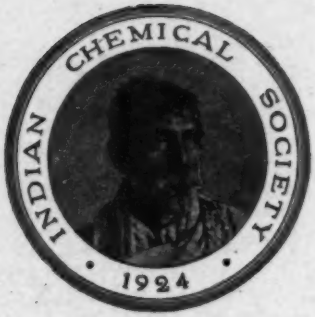

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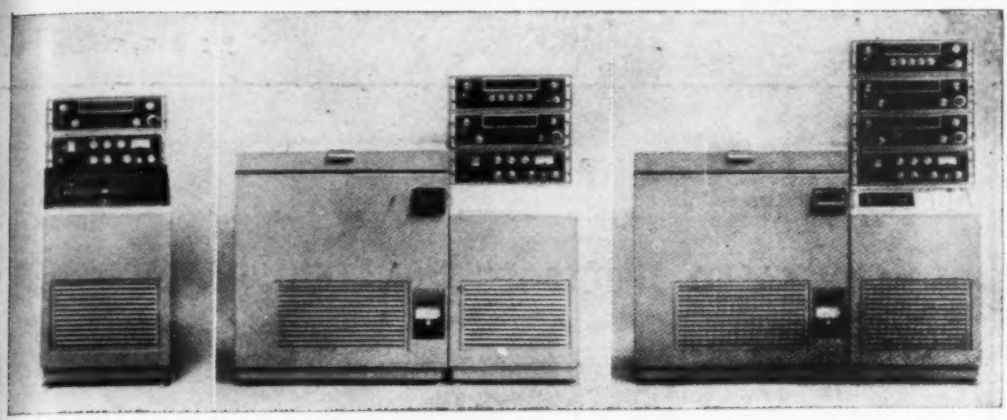

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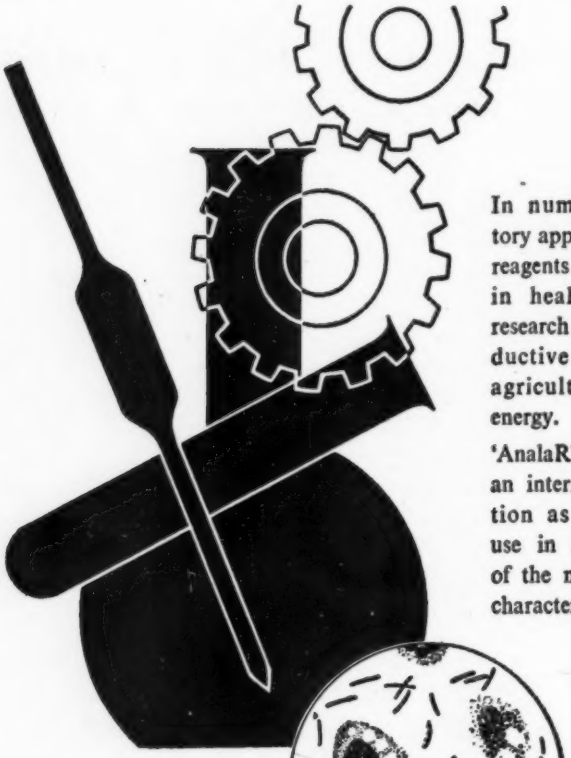

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[Jour. Indian Chem. Soc., Vol. 38, No. 10, 1961]

An Expression for the Evaluation of Partition Coefficient in Countercurrent Distribution

S. B. Ghosh, R. K. Sinha, and P. Nandi

The advantages and difficulties of the different methods for calculating K from the experimental distribution band have been discussed. A formula relating K with r_{max} and n has been deduced from the binomial relation without neglecting r_{max} in comparison with n, as Nichols did. The limitations of the formula, which holds good for K, much deviated from unity and at a comparatively small value of n, have been analysed in detail. The cause of deviation of the formula for a very high or low value of K has been explained. The formula approaches Craig's as n approaches ∞ or K approaches unity, *i.e.*, at the condition where binomial distribution approaches the Gaussian. The range of usefulness of the formula has been compared with Craig's considering the theoretical distribution patterns obtained from the B. P. D. Tables, as well as the experimental distribution bands of succinic acid between amyl alcohol and water ($K \ll 1$) and neutral red between butanol^n and 1% HCl ($K \ll 1$).

In order to calculate the theoretical distribution band, it is of primary importance to know the exact value of the partition coefficient of the distributed material. Besides, in case of a binary mixture, the partition coefficients of the individual components should be accurately known for the prediction of the degree of separation for a particular number of transfers. The preference of calculating K from the experimental distribution band to its determination from single partition study has been discussed by Craig and Craig ("Technique of Organic Chemistry", edited by Weissberger, 1950, Vol. III, pp. 171-311, Interscience Publishers, New York).

Of the different expressions concerning K (Craig, *J. Biol. Chem.*, 1944, **155,** 519; Williamson and Craig, *ibid.*, 1947, **168,** 687; Lieberman, *ibid.*, 1948, **173,** 63; Bacher, *J. Amer. Chem. Soc.*, 1951, **73,** 1023), mostly used is that of Craig.

$$K\, r_{max} = \frac{nK}{K+1} \qquad (1)$$

from which it follows:

$$K = \frac{r_{max}}{n - r_{max}} \qquad (2)$$

It is an approximate relation and becomes exact only if K is equal to 1 or if there is an infinite number of transfers (Williamson and Craig, *loc. cit.*). In case of a finite number of transfers and where the partition coefficient deviates considerably from unity on either side, the calculated K value deviates considerably from the actual; hence considerable trials are needed in order to fit the theoretical distribution curve with the experimental one. In these cases, the necessity of more accurate calculations based on binomial expansion has been recognised (Gregory and Craig, *Ann. N. Y. Acad. Sci.*, 1951, **53,** 1015).

The method due to Williamson and Craig (*loc. cit.*) has the advantage that the ratio of concentration in two adjacent tubes in any part of the distribution band can be used for the calculation of K. This method is suitable for the determination of K of individual components of a binary mixture from tubes lying on the slope of the distribution band when the peak regions do not contain pure solute or even resolution of the peaks is not effected. But the method fails to give accurate K value in case of heterogeneous solute, where the ratio of $T_{n,r}$ values in the two adjacent tubes does not correspond to the ratio of their total concentrations. This difficulty, however, may be removed if a highly specific analytical method of determination of the solute in question is available. The calculation of K according to Lieberman (*loc. cit.*) is easy to perform with a calculating machine. It should be noted here that Lieberman directly differentiated the logarithmic form of equation (3), viz.,

$$T_{n,r} = \frac{n!}{r!(n-r)!} \cdot \frac{1}{(K+1)^n} \cdot K^r \qquad (3)$$

with respect to r without assuming Stirling's approximation. Consequently, it is not possible to accommodate in his treatment the peak in the hypothetical fractional tube.

The method due to Bacher (*loc. cit.*) is statistically perfect and provides the best method of calculating K in the case of a homogeneous solute. But since all the tubes may not always contain pure solute, the experimental value of the first or the second mean cannot be accurately determined unless a highly specific analytical method of determination of the solute concerned is available. Unlike this method, the others require the solute to be pure either in the tubes at the peak region of the distribution band or in any two adjacent tubes.

The methods due to Williamson and Craig (*loc. cit.*), Lieberman (*loc. cit.*), and Bacher (*loc. cit.*) have no doubt an advantage over that due to the earlier method of Craig (*loc. cit.*) of determining K values from the distribution band even when the peak is attained in the oth or nth tube, but owing to its simplicity Craig's method is often preferred. Moreover, when the number of transfers is high, Craig's expression for K becomes exact, if K is not too high or too low. It is, of course, expedient to check the K value by calculating it directly from the analysis of the tube corresponding to the peak or any other region.

Theoretical Considerations

Nichols (*Anal. Chem.*, 1950, **22**, 915) deduced equation (1) from equation (3) and pointed out the approximations involved in the deduction. He differentiated the logarithmic form of equation (3), set the derivative equal to zero, and obtained equation (4), when $r = r_{max}$, the tube number where peak of the distribution band is reached.

$$\frac{n+0.5}{n} + \ln \frac{n}{n-r_{max}} - \frac{n-r_{max}+0.5}{n-r_{max}} + \ln \frac{1}{K+1} = 0 \qquad (4)$$

When n is large with respect to r_{max}, the first and the third terms in the left hand side of equation (4) cancel out and on simplification, equation (4) reduces to equation (1). The following points may be noted in connection with the above derivation:

(1) The formula given by Craig is an approximate one and becomes exact only when either n tends to infinity or K becomes unity (Williamson and Craig, *loc. cit.*). The first

condition justifies the omission of r_{max} in the third term of the left hand side of equation (4); but at $K=1$, r_{max} becomes $0.5n$, which cannot be neglected in comparison with n.

(2) When $K \gg 1$, r_{max} in equation (4) cannot be neglected in comparison with n and equation (1) does not hold good. But when $K \ll 1$, r_{max} in equation (4) can be neglected in comparison with n and equation (1) can be derived, but in this case equation (1) does not hold good as well. If r_{max} is put equal to zero, this would mean no distribution at all. This can also be seen by putting $r_{max}=0$ in equation (4), when K becomes equal to zero.

The above analysis clearly suggests that r_{max} must not be neglected in comparison with n if an exact value of K is desired. In view of this it is found expedient, following Lieberman (*loc. cit.*), to differentiate equation (3) with respect to r and not to n.

To do this, equation (3) is written in the form:

$$T_{n,r}=C.\frac{1}{r!}.\frac{K^r}{(n-r)!}$$

Where $C=\dfrac{n!}{(K+1)^n}$ is constant.

Taking logarithms,

$$\ln T_{n,r} = \ln C - \ln r! + r\ln K - \ln(n-r)!$$

Using Stirling's approximation,

$$\ln T_{n,r} = \ln C - 0.5\ln 2\pi - (r+0.5)\ln r + r + r\ln K - 0.5\ln 2\pi - (n-r+0.5)\ln(n-r) + n - r.$$

Differentiating with respect to r, n remaining constant,

$$\frac{d\ln(T_{n,r})}{dr} = \ln K - \ln\frac{r}{n-r} + \frac{r-0.5n}{r(n-r)} \quad \ldots\ldots \quad (5)$$

Setting the derivative equal to zero, when $r=r_{max}$, and rearranging

$$\ln K = \ln\frac{r_{max}}{n-r_{max}} - \frac{r_{max}-0.5n}{r_{max}(n-r_{max})}$$

$$K = \frac{r_{max}}{n-r_{max}} . e^{-(r_{max}-0.5n)/r_{max}(n-r_{max})} \quad \ldots\ldots \quad (6)$$

That r_{max} is the tube number, where the maximum of the distribution curve lies, can be shown by differentiating equation (5) with respect to r and rearranging.

$$\frac{d^2(\ln T_{n,r})}{dr^2} = \frac{-r(n-r)(1+n) + 0.5n^2}{r^2(n-r)^2} \quad \ldots\ldots \quad (7)$$

If this value of r should represent r_{max}, the second derivative ought to be negative. The denominator of the right hand side of the equation involving square terms is always positive. As $r > n$, the first term of the numerator is always negative; the second term is always positive. The limiting value of r, for which the numerator becomes negative, should be

such as to give amongst others a $-0.5n^2$ term. This can be achieved by substituting r either by 0.5 or $(n-0.5)$. In either case, equation (7) is reduced to

$$\frac{d^2(\ln T_{n,r})}{dr^2} = \frac{1-n}{(n-0.5)^2} \qquad (8)$$

Since for a binomial distribution n should be at least 2, equation (8) is always negative.

But if r is substituted either by $0.5-x$ or $n-(0.5-x)$ where $x \gg 0.5$ (*i.e.*, at the limiting value of x, r is either equal to 0 or n), equation (7) is reduced to

$$\frac{d^2(\ln T_{n,r})}{dr^2} = \frac{-0.25n+025-x+x^2+n^2x+nx^2}{(0.5-x)^2\{n-(0.5-x)\}^2} \qquad (9)$$

The right hand side, as can be easily shown, is always positive for any value of x within its limiting value, *i.e.* 0.5.

The above analysis therefore shows that the second derivative of $\ln T_{n,r}$ (cf eq. 7) is negative, *i.e.*, a maximum will occur only if $(n-0.5) \gg r \gg 0.5$. Consequently, calculation of K based on r_{max} with the help of equation (6) is significant if r_{max} occurs within the above range, viz., $(n-0.5)$ and 0.5. Unlike equation (1) or (2), equation (6) has been derived, using Stirling's approximation, but without neglecting r_{max} compared to n and is therefore more exact.

Moreover, equation (6) reduces to equation (2) if the exponential term is unity, or in other words, the exponent is zero. This is so, if $r_{max} = n/2$ or $n = \infty$, which would respectively mean that $K=1$ and n is large. These are exactly the conditions under which equation (2) becomes exact. Equation (6), which is based only on the condition: $(n-0.5n) \gg r \gg 0.5$, is therefore expected to be more accurate, as shown by the data recorded in Tables I and II.

TABLE I

Comparison of the theoretical and the calculated K values.

Number of transfers, $n = 24$.

p.	r_{max}.	K (B.P.D. Tables).	K (eq. 6).	K (eq. 2).	p.	r_{max}.	K (B.P.D. Tables).	K(eq.6).	K(eq.2).
0.04	0.5	0.0417	0.0566	0.0213	0.52	12.5	1.0833	1.0832	1.0879
0.08	1.5	0.0870	0.0910	0.0667	0.56	13.5	1.2727	1.2722	1.2857
0.12	2.5	0.1364	0.1388	0.1163	0.60	14.5	1.5000	1.4989	1.5263
0.16	3.5	0.1905	0.1922	0.1707	0.64	15.5	1.7778	1.7757	1.8235
0.20	4.5	0.2500	0.2514	0.2308	0.68	16.5	2.1250	2.1214	2.2000
0.24	5.5	0.3158	0.3169	0.2973	0.72	17.5	2.5714	2.5651	2.6923
0.28	6.5	0.3889	0.3898	0.3714	0.76	18.5	3.1667	3.1554	3.3636
0.32	7.5	0.4706	0.4714	0.4545	0.80	19.5	4.0000	3.9782	4.3333
0.36	8.5	0.5625	0.5632	0.5484	0.84	20.5	5.2500	5.2026	5.8571
0.40	9.5	0.6667	0.6671	0.6552	0.88	21.5	7.3333	7.2071	8.0000
0.44	10.5	0.7857	0.7861	0.7778	0.92	22.5	11.5000	10.9897	15.0000
0.48	11.5	0.9231	0.9232	0.9200	0.96	23.5	24.0000	17.6626	47.0000
0.50	12.0	1.0000	1.0000	1.0000					

TABLE II

Comparison of the theoretical and the calculated K values.

Number of transfers, $n = 49$.

p.	r_{max}.	K (B.P.D. Tables).	K(eq.6).	K(eq.2).	p.	r_{max}.	K (B.P.D. Tables).	K(eq.6).	K(eq.2).
0.02	0.5	0.0204	0.0277	0.0103	0.50	24.5	1.0000	1.0000	1.0000
0.04	1.5	0.0417	0.0436	0.0316	0.52	25.5	1.0833	1.0833	1.0851
0.06	2.5	0.0638	0.0650	0.0538	0.54	26.5	1.1739	1.1738	1.7778
0.10	4.5	0.1111	0.1117	0.1011	0.58	28.5	1.3810	1.3808	1.3902
0.14	6.5	0.1628	0.1632	0.1529	0.62	30.5	1.6316	1.6313	1.6486
0.18	8.5	0.2195	0.2199	0.2099	0.66	32.5	1.9412	1.9404	1.9697
0.22	10.5	0.2821	0.2823	0.2727	0.70	34.5	2.3333	2.3322	2.3793
0.26	12.5	0.3514	0.3516	0.3425	0.74	36.5	2.8462	2.8442	2.9200
0.30	14.5	0.4286	0.4288	0.4203	0.78	38.5	3.5455	3.5420	3.6667
0.34	16.5	0.5152	0.5153	0.5077	0.82	40.5	4.5556	4.5483	4.7647
0.38	18.5	0.6129	0.6130	0.6066	0.86	42.5	6.1429	6.1258	6.5385
0.42	20.5	0.7241	0.7242	0.7193	0.90	44.5	9.0000	8.9487	9.8889
0.46	22.5	0.8519	0.8519	0.8491	0.94	46.5	15.6667	15.3938	18.6000
0.48	23.5	0.9231	0.9231	0.9216	0.96	47.5	24.0000	22.9306	31.6667
					0.98	48.5	49.0000	36.0539	97.0000

DISCUSSION

Tables I and II present the values of K calculated according to equations (2) and (6) for different values of r_{max}, as shown in the B. P. D. Tables ("Tables of the Binomial Probability Distribution", National Bureau of Standards, Applied Mathematics Series, Washington) for 24 and 49 transfers respectively. The calculated K values are compared with those evaluated from the values of p provided in the B. P. D. Tables (Way and Bennett, *J. Biol. Chem.*, 1951, **192**, 335). All the K values are rounded up to the fourth place of decimal. A slight defect in drawing the experimental curve may change the exact position of the peak in the hypothetical fractional tube and thus change the calculated K values considerably. This difficulty has been removed by choosing only those distribution values from the B. P. D. Tables where two successive tubes give the same value of the distributed material and the peak is assumed to be situated in between the two tubes. But when fractions in the two tubes separated by a single tube have the same value, the peak is assumed to be half way between the two.

For example, when $n=24$ and $p=0.20$ (*i.e.*, $K=0.25$), it is seen from the B. P. D. Tables that the fractions distributed at $r=4$ and $r=5$ have the same value, viz., 0.1960151. Hence r_{max} is taken as 4.5. Now substituting the values of n and r_{max} in equation (6), $K=0.23077.e^{0.08547}=0.2514$. It will be observed that the K values calculated from equation (6) is in better agreement with those in the B. P. D. Tables than those calculated from equation (2).

For values of $K>1$, *i.e.*, $p>0.5$, equations (2) and (6) are replaced by equations (2a) and (6a) respectively (cf. Way and Benett, *loc. cit.*).

$$K = \frac{n - r_{max}}{r_{max}} \quad .. \quad .. \quad (2a)$$

$$K = \frac{n - r_{max}}{r_{max}} \cdot e^{-(0.5\, n\, -r_{max})/r_{max} \cdot (n\, -\, r_{max})} \quad .. \quad (6a)$$

Here also the agreement between the values calculated with equation (6a) and B. P. D. Tables is much better than that with equation (2a). At higher values of p or K, the agreement is poor. A comparison of Tables I and II shows that the difference between the two equations becomes less, when $n=49$, than when $n=24$. Furthermore, the difference between equations (2) and (2a) and B. P. D. Tables is much wider at lower and higher values of r_{max} compared to the corresponding difference between equations (6) and (6a) and B. P. D. Tables. The difference is less and less as $p \rightarrow 0.5$, *i.e.*, $r_{max} \rightarrow n/2$, or $K \rightarrow 1$. At $p=0.5$, or $r_{max}= n/2$, or $K=1$, all the K values are obviously identical.

It may be noted that Stirling's approximation should be assumed only for high numbers. In case of the logarithmic form of equation (3), assumption of the same approximation introduces considerable error when r approaches 0 and n, for then the magnitudes of r and $(n-r)!$ become small. In equation (2) this inaccuracy is combined with the inaccuracy of neglecting r_{max} in comparison with n, specially when r_{max} approaches n.

The limiting values of r_{max}, *i.e.*, 0.5 and $(n-0.5)$, show the limiting values of K, which can be calculated with the help of equation (6) for a particular number of transfers. Tables I and II show that the ranges of values of K are from 0.0566 to 17.6626 for $n=24$ and 0.0277 to 36.0529 for $n=49$. This suggests that in order to obtain a theoretical curve for a substance having a very high or low partition coefficient, the number of transfers applied should be sufficiently high. Again, the limiting values of K are expected to have a maximum deviation from the corresponding actual K values. But the limiting values of K for a particular number of transfers applied deviate more and more from the limiting values of K as the number of transfers applied becomes higher and higher. Thus higher the number of transfers applied for a solute having very low or high K values, the more accurate should be its theoretical curve.

As the binomial distribution is a statistical distribution, the applicability of equations (2) and (6) may be discussed from the statistical viewpoint. If a unimodal distribution can be fitted with a smooth frequency curve, the mode is defined as the abscissa of the highest point on the curve, *i.e.*, r_{max} in countercurrent distribution curve. But for a binomial distribution, the mean number of success, *i.e.*, the mean position of the distribution curve is equal to the probability of success, p, in a single trial multiplied by the number of trials, n (cf. Bock, *J. Amer. Chem. Soc.*, 1950, **72**, 4269), that is,

$$m = np = \frac{nK}{K+1} \quad .. \quad (10)$$

Craig equated the mode of distribution with its mean position, which is only true for a symmetrical distribution, *i.e.*, when K is equal to 1 or n is infinity. Bacher (*loc. cit.*) equated the observed and the theoretical mean of binomial distribution to evaluate K. But equation (6) is deduced on the basis of equality of the theoretical and the observed mode of binomial distribution. In fact, the observed mode, r_{max}, is not evaluated as it is difficult to solve for r_{max} in equation (6). Hence equation (6), like that of Bacher, is sound from the statistical viewpoint.

Like all other equations relating K, equation (6) cannot give an accurate value of K if the peak region is not homogeneous. In that case a highly specific method of analysis of the solute concerned is essential. Notwithstanding this difficulty, equation (6) should be helpful in the calculation of K values much deviated from 1 on either side of a comparatively small number of transfers, where equation (2) fails.

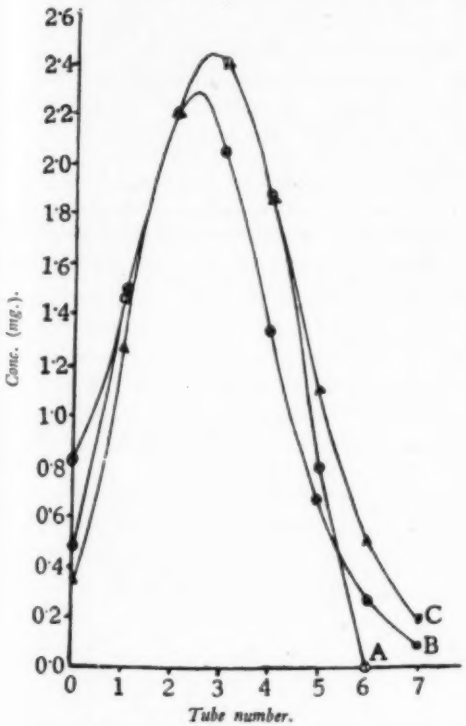

FIG. 1.
A—experimental.
B—theoretical (K from eq. 2)
C— " (K from eq. 6)

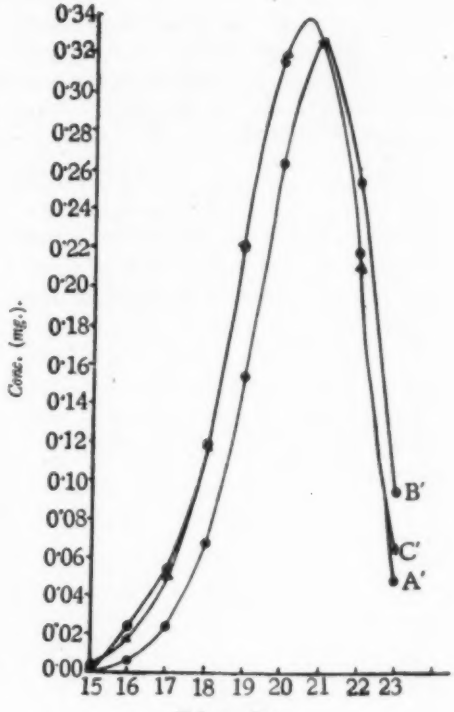

FIG. 2.
A′—experimental.
B′—theoretical (K from eq. 2).
C′— " (K from eq. 6).

In order to test the validity of equation (6), two solutes were so chosen that K of one was much less and that of the other much greater than unity. In Fig. 1, curve A gives an experimental distribution band of 10 mg. of succinic acid distributed between water and amyl alcohol. The fractions were analysed by titration with $N/30$-NaOH solution and r_{max} was found to be 2.7. Curves B and C are theoretical curves calculated on the basis of $K=$ 0.13300 and 0.15618 according to equation (2) and (6), respectively. In Fig. 2, curve A′ shows an experimental distribution band of 1.3 mg. of neutral red distributed between butanol[n] and 1% HCl solution. The fractions were analysed spectrophotometrically (max. absorption at 540 mμ). r_{max} was found to be 20.6. Curves B′ and C′ are the theoretical curves calculated on the basis of $K=8.5835$ and 7.1402 according to equations (2) and (6), respectively. 23 transfers were used in both. Absolute ethanol was used as co-solvent in both the cases.

It is seen that curves C and C′ have a closer agreement with curves A and A′ respectively than with curves B and B′. The deviations in the trailing parts of the curves are probably due to the non-linearity of the partition isotherm of the solute distributed. In Fig. 2, curve B′ only touches curve A′ at the point corresponding to the 21st tube where it is fitted. In Fig. 1, though the peak of curve A falls at a hypothetical fractional tube, $r_{max} = 2.7$, due to the drawing of a smooth curve, tube number 3 will in reality have the maximum concentration of the distributed material. Curve C has also the maximum concentration of the solute in tube number 3, but curve B surprisingly enough has maximum concentration in tube number 2. Moreover, curves B and B′ fail to reproduce the peaks in the hypothetical tubes of their corresponding experimental distribution, since they are fitted in the position of the peaks of the real tubes.

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Studies on Stereochemical Reaction in Heterocyclic Compounds. Part II. Stereochemical Conversion of Yohimbine to β-Yohimbine*

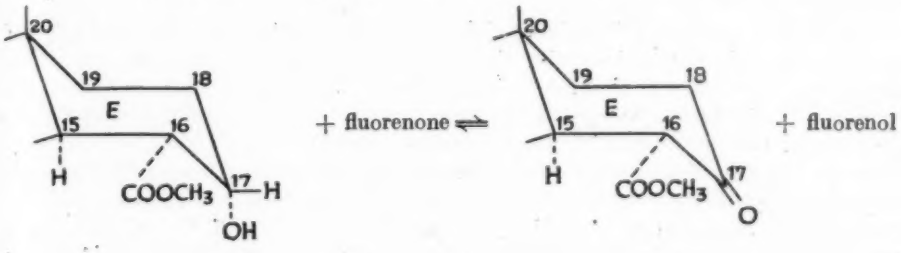
Mrs. A. Chatterjee and S. Ghosal

Epimerization of yohimbine to β-yohimbine has been achieved in presence of alkoxide ions and carbonyl reagents in hydroxylic and nonpolar solvents. This steric change is explainable by a two-step mechanism.

In an earlier publication (Chatterjee and Ghosal, this *Journal*, 1959, **36**, 545), studies on the behaviour of yohimbone and rauwolscone towards complex metal hydrides were reported. The present communication describes the steric course of epimerization of yohimbine to β-yohimbine in presence of basic catalysts and hydrogen acceptors in non-polar and hydroxylic solvents. The proposed mechanism of stereochemical conversion has been found to be consistent with the experimental evidences and is similar to that proposed by Doering and his associates (*J. Amer. Chem. Soc.*, 1947, **69**, 1700).

Based on this concept, we have been able to equilibrate yohimbine and obtained β-yohimbine under varying experimental conditions.**

The first step of this reaction is assumed to involve oxidation of yohimbine (I) to yohimbinone (II) by a carbonyl compound, e.g., fluorenone in presence of alkali alkoxides.



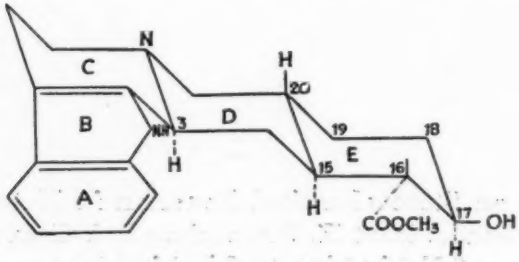
(I) (II)

This reaction is thus similar to oxidation-reduction equilibrium between alcohol-ketone systems catalysed by an alkoxide ion (Ponndorf, *Angew. Chem.*, 1926, **39**, 138).

Subsequent conversion of the ketone (II) to β-yohimbine (III) involves either its stereospecific reduction with sodium borohydride (Chatterjee *et al.*, *loc. cit.*) or its reduction by alkoxide ions in corresponding alcoholic solvents to yield the more stable epimer (III).

* Addendum: Since the communication of this paper a publication on similar studies (Janot, Goutarel, Warnhoff, and Le Hir, *Bull. Soc. Chim.*, 1961, **3**, 637) has appeared.

** cf. Ghosal and Chatterjee, *Proc. Ind. Sci. Cong.*, 1960, Part III, 143.



(III)

This second operation in conjunction with the previous one completes the epimerization of yohimbine to β-yohimbine.

Reduction of ketones by alcohols in presence of alkoxides is well known ("Meerwein-Ponndorf reduction", A. L. Wilds, "Organic Reactions", Vol. II, J. Wiley & Sons, N.Y., 1944, p. 178). Besides, there are a number of references in which sodium alkoxide effects reduction of ketones (Rubin, *J. Amer. Chem. Soc.*, 1944, **66,** 2075). Transformation of yohimbinone to β-yohimbine, as stated above, is an exemplification of these observations (*loc. cit.*).

It was found (Doering *et al.*, *loc. cit.*) that carbonyl compounds (capable of producing diastereomeric alcohols) on reduction with alcohols in presence of the corresponding alkoxides gave a mixture of epimers. Yohimbinone behaved similarly and yielded a mixture of yohimbine and β-yohimbine when reduced under similar conditions. The mixture thus obtained was subsequently separated into two homogeneous components by chromatographic resolution.

In further support of the validity of the proposed oxidation-reduction mechanism of equilibration might be mentioned the behaviour of quinine and quininone (Doering *et al.*, *loc. cit.*) towards tertiary alcohols. According to the mechanism cited above, ketones should be incapable of reduction by tertiary alcohols, the latter being incapable of oxidation by the ketones. In consonance with this conclusion, quininone was found to be completely stable in a solution of potassium butoxide^t in butanol^t under reflux condition. Despite several other instances, which support this generalisation, yohimbine was claimed to undergo a single-step epimerization to β-yohimbine (Le Hir and Warnhoff, *Compt. rend.*, 1958, **246,** 1564) with potassium butoxide^t in dry benzene. We could not, however, effect such equilibration under similar experimental conditions. In fact, only a sluggish disproportionation was observed when yohimbine was refluxed with this alkoxide in the corresponding alcohol, resulting in a small amount of yohimbinone (1.02%).

Another important factor that has been considered for the degree of the above transformation (I-III) is the role of carbonyl reagents. Fluorenone exhibited a definite improvement over benzophenone. Thus, boiled for 45 hours with 1, 2, and 5 equivalents of the latter in a solution of sodium methoxide in benzene, yohimbine was converted to yohimbinone in yields of 3, 5, and 8% respectively. When similarly treated with 2 equivalents of the rapid oxidising agent, like fluorenone, yohimbine produced the desired ketone in 70% yield.

An interesting difference in the rate of oxidation (I-II) was also observed when sodium was replaced with potassium. The formation of yohimbinone (70%) in presence of sodium methoxide required 20 hours, whereas the optimum time for oxidation was only 8 hours with the corresponding potassium alkoxide. Since the transformation reaction requires catalytic action of strong bases (Doering *et al.*, *loc. cit.*), the increased rate of reaction in presence of potassium alkoxide may be ascribed to the weaker conjugate acidity of the potassium ion in comparison with the more acidic sodium ion.

EXPERIMENTAL

Oxidation of Yohimbine to Yohimbinone.—A mixture of yohimbine (0.5 g.), sodium methoxide (0.1 g.), and fluorenone (0.2 g.) in dry benzene (500 c.c.) was refluxed for 20 hours when yohimbinone sodium enolate separated from the reaction mixture. The reaction mixture was then cooled, poured into ice, and extracted with 5% HCl (40 c.c.). The acid extract was cooled in ice and basified with ice-cold liquor ammonia (*p*H 7.5—8). Yohimbinone, precipitated as a pale yellow solid, was extracted with chloroform. The aqueous layer was salted and re-extracted with chloroform. The combined chloroform extracts (150 c. c.) were washed with water (saturated with sodium chloride), dried, and evaporated on a water bath (0.42 g.). The residue was crystallised from ethanol in long, pale yellow needles, m.p. 255-56° (decomp.). (Found in a dry sample: C, 71.48; H, 7.33; N, 7.78. $C_{21}H_{24}O_3N_2$ requires C, 71.39; H, 6.82; N, 7.95%).

The above process of oxidation was repeated with several other alkoxides and carbonyl reagents. The results obtained from these operations have already been recorded (*vide supra*).

2, 4-Dinitrophenylhydrazone of Yohimbinone.—To a solution of yohimbinone (50 mg.) in aldehyde-free ethanol (20 c. c.) was added a solution of 2, 4-dinitrophenylhydrazine sulphate (20 mg.) in the same solvent (10 c.c.). The mixture was concentrated when D.N.P.H. of yohimbinone separated. Crystallisation from ethanol yielded orange-red needles, m.p. 288-90°. (Found in a dry sample: N, 15.42. $C_{27}H_{28}O_6N_6$ requires N, 15.78%).

Reduction of Yohimbinone to β-Yohimbic Acid.—To a well-cooled solution of yohimbinone (0.2 g.) in moist methanol (50 c. c.) a solution of sodium borohydride (0.1 g.) in the same solvent (dry) was slowly added. The solution was kept at room temperature overnight. On removing the solvent a residue was left which was subsequently decomposed with ice-cold water (10 c. c.) and then acidified with acetic acid (*p*H 5.5.-6.0). The mixture was extracted with ether (25 c. c. × 4). Ether extract was washed with water, dried, and concentrated. Crude residue on crystallisation from methanol gave pure β-yohimbic acid, m.p. 261-63°. (Found in a dry sample: C, 70.36; H, 7.20; N, 8.43. Calc. for $C_{20}H_{24}O_3N_2$: C, 70.60; H, 7.06; N, 8.23%).

Esterification of β-Yohimbic Acid to β-Yohimbine.—Crude β-yohimbic acid (0.1 g.) was dissolved in dry methanol (50 c.c.), cooled in a freezing bath, and dry HCl gas was passed through it till saturation. The solution was kept at room temperature overnight. It was then warmed on a steam bath to expel excess of HCl gas and the solvent was removed under suction. Crystallisation of the corresponding base from methanol yielded β-yohimbine (50 mg.), m.p 237-38°. Mixed m.p. with an authentic sample of β-yohimbine, $2CH_3OH$ remained undepressed. (Found in a dry sample: C, 71.04; H, 7.18; N, 7.82. Calc. for $C_{21}H_{26}O_3N_2$: C, 71.18; H, 7.34; N, 7.90%).

Reduction of Yohimbinone with Alkoxides.—Yohimbinone (200 mg.) was gently refluxed in a solution of dry sodium ethoxide (1 g.) in absolute ethanol (50 c.c.) for 15 hours. The solvent was removed in *vacuo* and the residue triturated with 5*N*-HCl (25 c.c.). The aqueous acid solution was then basified and extracted with chloroform (20 c.c.×3). The chloroform extract was washed with water, dried to a small volume, and concentrated. The mixture of crude bases separating was purified by chromatographic resolution over Brockmann alumina (2 g.) using a mixture of methanol and acetone as the solvent and the eluent as well. The eluates were collected in fraction of 25 c. c. portions and evaporated to dryness (Table I).

TABLE I

Eluents.	Fraction collected.	Residue.	$[\alpha]^{28}$ (pyridine).
Acetone 98% Methanol 2	1—5	Negligible	..
Acetone 95% Methanol 5	6—9	Yohimbine (85 mg.) m.p. 232°	+98±1°
Acetone 80% Methanol 20	10—15	β-Yohimbine (78 mg.) m.p. 238°	−53±1°

The above experimental method for the reduction of yohimbinone to β-yohimbine was adopted with other alkoxides resulting in varying degrees of success (*vide supra*).

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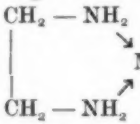
Studies in Metallic Complexes of Ethylenediamine Hydrochloride. Part I. Complex Formation between Vanadyl Sulphate and Ethylenediamine Hydrochloride

P. K. Bhattacharya, M. C. Saxena, and S. N. Banerji

Vanadyl sulphate forms a water-soluble complex with ethylenediamine hydrochloride. The composition of the complex, established spectrophotometrically and conductometrically by the application of Job's method of continued variations, has been found to be VOR_2 (R=reagent). The dissociation constant of the complex at 20° is 2×10^{-6}.

The ethylenediamine molecule, $H_2N\text{-}CH_2\text{-}CH_2\text{-}NH_2$, is remarkable for its power of forming a stable five-membered ring of the type



(M=metal ion).

Chelates between ethylenediamine and trivalent transitional atoms such as Cr^{3+} (Rollinson and Bailar, *J. Amer. Chem. Soc.*, 1943, **65**, 250), Fe^{3+} (Breuil, *Compt. rend.*, 1933, **196**, 2009), and Co^{3+} (Jaeger and Blumendal, *Z. anorg. Chem.*, 1928, **175**, 161) have been reported. With the divalent cupric atom, 6-covalent complexes of this kind are known, but a more usual and exceptionally stable (Job, *Compt. rend.*, 1927, **184**, 1066) type is the 4-covalent dichelate form. Such ring structures are also met with in the case of other bivalent metals, viz., Be^{2+} (Fricke and Havestadt, *Z. anorg. Chem.*, 1924, **152**, 357), Zn^{2+}, and Cd^{2+} (Hieber and Reindl, *Z. Elektrochem.*, 1940, **46**, 556.)

Vanadium in vanadyl (VO^{2+}) state is known to give rise to 4-covalent complexes with bidentate ligands (Zolotavin and Kalugina, *Zhur. neorg. Khim.*, 1950, **1**, 703; Bhattacharya and Banerjee, *Curr. Sci.*, 1960, **29**, 147). The present investigation was undertaken with a view to studying the system vanadyl sulphate and ethylenediamine hydrochloride by using spectrophotometric, conductometric, and *p*H methods.

EXPERIMENTAL

Solutions of vanadyl sulphate (B.D.H.) and ethylenediamine hydrochloride (AnalaR) in conductivity water were used. The vanadium (IV) content of the vanadyl sulphate solution was estimated before use by means of ammonium benzoate as a precipitant (Shemyakin and Chapuigin, *J. Appl. Chem., U.S.S.R.*, 1935, **8**, 536). Beckman spectrophotometer, Doran conductivity bridge, and glass electrode *p*H meter were used for optical density, conductance, and *p*H measurements, respectively. The measurements were carried out at a constant temperature of $20^\circ \pm 0.1^\circ$.

Nature of the Complex Formed

The absorption spectra of mixtures of equimolar solutions ($M/10$) of vanadyl sulphate and the reagent in the ratios of 1:1, 1:2, and 1:3 were studied. The nature of the curves (Fig. 1, curves A, B, & C) is identical; moreover, they do not intersect each other, thus indicating the probability of the formation of only one complex. The curves show maxima at the wave length of about 775 mμ. For further study, the optical density measurements were taken at or near this wave length.

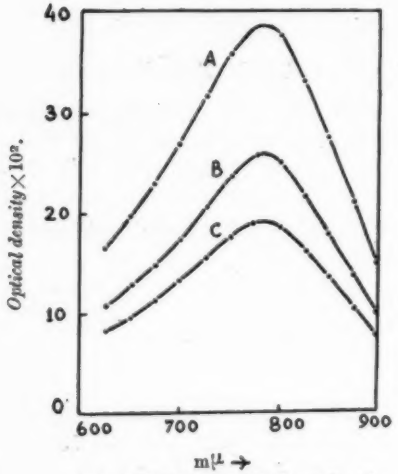


FIG. 1. Variation of O. D. with mμ.
A : 1:1 mixture
B : 1:2 „
C : 1:3 „

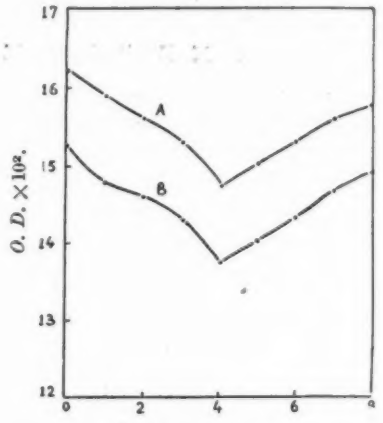


FIG. 2. Comp. of the complex by monovariation method.
A : 775 mμ.
B : 750 mμ.

The nature of the complex has been further studied by the application of monovariation method (Nayar and Pandey, *Proc. Ind. Acad. Sci.*, 1948, **27A,** 284). Only one break, at 1:2 ratio, is seen in the curves obtained from optical density (Fig. 2, curves A & B), conductance, and *p*H (Fig. 3, curves A & B) measurements showing the formation of only one complex.

Effect of H^+ *Ion Concentration on the Absorption of Light*

The absorbance of a mixture of equimolar ($M/10$) vanadyl sulphate and ethylenediamine hydrochloride in the ratio of 1:2 at wave length 775 mμ was noted over a *p*H range of 2 to 5. The results indicate that the colour intensity reaches a maximum at *p*H 4 and then decreases at higher *p*H values. Therefore optical measurements were taken with solutions having *p*H 4.

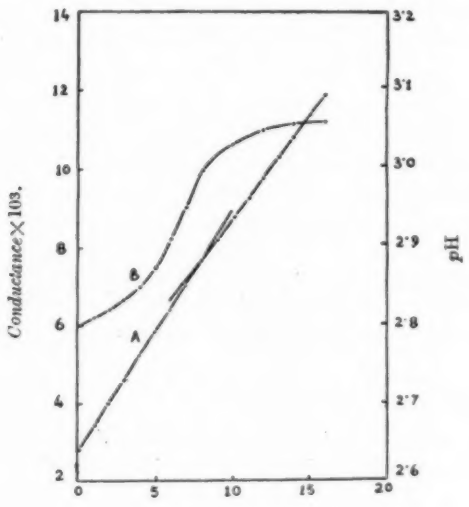


FIG. 3 Composition of the complex by monovariation method.
A : by conductance.
B : by *p*H.

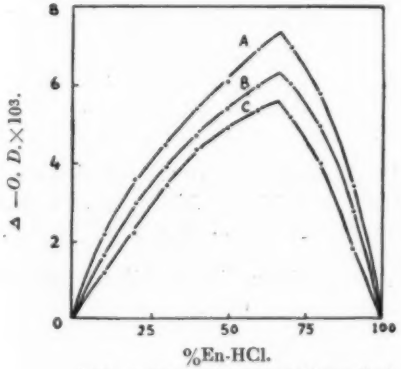


FIG. 4. Composition by Job's method.
A : at 775 mμ
B : „ 750 „
C : „ 800 „

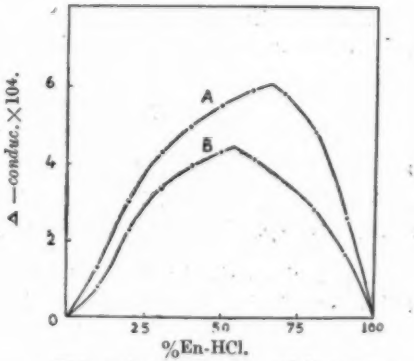


FIG. 5. Composition (A) and diss. const. (B) of the complex.

Composition of the Complex by Job's Method : Spectrophotometric Study

The composition of the complex formed was determined by Job's method of continued variation (*Ann. chim.*, 1928, *x*, **9**, 113), using *M*/10 solutions each of vanadyl sulphate and ethylenediamine hydrochloride. The optical densities were noted at wave lengths 750 mμ, 775 mμ, and 800 mμ. In all the cases the maxima in the curves plotted (Fig. 4, curves A, B, & C)

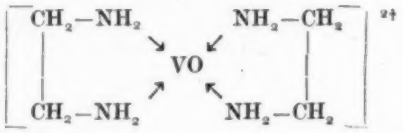
between the difference in optical density and percentage of ethylenediamine hydrochloride were obtained at 66% ethylenediamine hydrochloride, indicating the formation of a 1:2 complex.

Conductometric Study.—The stoichiometry of the complex formed was confirmed by the application of Job's method (*loc. cit.*) to conductance measurements using equimolar (*M*/40) solutions of vanadyl sulphate and ethylenediamine hydrochloride. The curve (Fig. 5, curve A) exhibits a maximum at 66% of ethylenediamine hydrochloride, establishing the stoichiometry of the complex as obtained from optical density measurements.

The dissociation constant of the complex formed was determined by conductometric measurement using nonequimolar solutions (*M*/60 vanadyl sulphate and *M*/40 ethylenediamine hydrochloride) in continued variation method.

DISCUSSION

The stoichiometry of the complex formed indicates that one molecule of vanadyl sulphate reacts with two molecules of ethylenediamine hydrochloride and it is represented as



The dissociation constant of the complex formed was calculated by substitution of the values in Job's simplified equation:

$$K = \frac{C^2.P\,[(P+2)\,x-2]^3}{(P-1)^2.\,(2-3x)}$$

where C=concentration of the metal solution, P=concentration of the ligand, and x= fraction of the ligand used. Thus, $C=M/60=0.01667$; $P=(M/40)/(M/60)=1.5$; $x=0.59$ (Fig. 5, curve B). The value of the dissociation constant K is found to be 2×10^{-6} at 20°.

The authors' thanks are due to Prof. A. K. Bhattacharya, Head of the Department of Chemistry, University of Saugar, for his keen interest in the work.

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Stepwise Stability Constants of Cadmium Complexes of Pyridine, β-Picoline, and γ-Picoline

A. G. Desai and M. B. Kabadi

The stepwise stability constants for the cadmium complexes of pyridine, β-picoline, and γ-picoline have been evaluated from the E. M. F. data, utilising the graphical method of Leden. The values for individual complexes with Cd: ligand ratio from 1:1 to 1:3 are as follows:

Cd—pyridine	:	$\beta_1=18$,	$\beta_2=90$,	$\beta_3=195$;
Cd—β-picoline	:	$\beta_1=25.5$,	$\beta_2=146$,	$\beta_3=345$;
Cd—γ-picoline	:	$\beta_1=31.5$,	$\beta_2=147$,	$\beta_3=941$.

The constants have been calculated for aqueous solutions of ionic strength 0.1 at 30°. Similar studies with α-picoline show that if any complexes are formed, they are very weak, probably due to steric hindrance of the $-CH_3$ group.

Sufficient data are available on the formation constants of metal complexes of aliphatic amines. It is noteworthy, however, that the aromatic amines do not seem to have received much attention from this point of view. Bjerrum, Schwarzenbach, and Sillén ("Stability Constants. Part I. Organic Ligands", the Chemical Society, London, 1957) have recorded a few data on the metal complexes of pyridine and only Ag^+-complexes of its derivatives. Euler (*Ber.*, 1904, **37**, 2768), Bailar *et al.* (*J. Amer. Chem. Soc.*, 1950, **72**, 2484), Morinaga (*Nippon Kagaku Zasshi*, 1956, **77**, 865), and Liu and Fu (*K'o Hsüeh T'ung Pao*, 1957, **23**, 718) have determined solution stability constants of Cd^{2+}—pyridine complexes. These results, however, are found to be controversial. The present communication deals with studies in the stepwise stability constants of cadmium complexes of pyridine, β-picoline, and γ-picoline in aqueous medium, utilising a method suggested by Leden (*Z. physikal. Chem.*, 1941, **A188**, 160).

EXPERIMENTAL

0.1*M*-$Cd(ClO_4)_2$ solution was prepared by dissolving $CdCO_3$ (E.Merck, extra pure) in 0.2*M*-$HClO_4$ solution, the former being added to latter till excess of $CdCO_3$ remained undissolved. The resulting solution was boiled and filtered. The Cd^{2+} ion concentration was estimated as $Cd_2P_2O_7$ by the usual method. Approximately 1.0*M* solution of $NaClO_4$ (E. Merck, pure grade) was prepared. Pyridine and picolines (B.D.H., pure grade) were distilled and from the distillate 1.0*M* solutions of picolines and 2.0*M* solution of pyridine were prepared. In the preparation of all these solutions, freshly prepared double-distilled water, free from CO_2, was used. The standardisation of these solutions was carried out potentiometrically, using a standard HCl solution.

Procedure.—The H-type cell, in which the middle compartment was separated by two sintered bed discs, was employed for the determination of the E. M. F. of the different conc. cells, prepared as follows:

	0.01*M*-$HClO_4$	Agar-agar	C_M -$Cd(ClO_4)_2$	
Pt^+	0.09*M*-$NaClO_4$	saturated with	0.1*M*-$NaClO_4$	$Cd\text{-}Hg^-$
	Quinhydrone	$NaClO_4$	C_L — ligand	

The right hand compartment consisted of a ligand, Cd^{2+} ions, 1.0m*M* in strength, and 0.1*M*-$NaClO_4$ solution for keeping ionic strength constant. The different solutions used were prepared by adequately diluting the corresponding stock solutions. The liquid cadmium amalgam, used as an electrode, was prepared by the method described by Vogel ("A Text-book of Quantitative Inorganic Analysis", p. 317, 2nd ed., Longmans, Green and Co.) and was preserved under 2.0*M*-H_2SO_4 solution. A portion of this was always washed before use with oxygen-free distilled water and dried with an absorbent paper. It was then immediately poured into right-hand compartment. The necessary precautions were taken to make this compartment completely free of oxygen by incessantly passing oxygen-free nitrogen through the solution for about 20 minutes so that the amalgam never came in contact with oxygen during the experiment. The left-hand side consisted of quinhydrone electrode in 0.01*M* perchloric acid and the middle compartment was filled with an agar-agar solution saturated with $NaClO_4$.

A series of readings of the E. M. F. of the combination, prepared as described before, were taken on 'PYE' potentiometer of sensitivity 0.1 mV at various concentrations of the ligands, keeping Cd^{2+} ion concentration constant. The accuracy of the experimental measurements is within ± 0.1 mV. The data were collected at a constant temperature of $30^\circ \pm 0.1^\circ$, using water thermostat controlled by a toluene regulator.

The E. M. F. of such a cell is given by

$$E = E' - \frac{RT}{nF} \ln [M].$$

where E' includes the potential of reference electrode, the liquid junction potential, and a contribution due to activity of metal ions in amalgam electrode and activity coefficients. All the factors were assumed to remain constant throughout the measurements.

When $C_L = 0$, *i.e.*, no ligand is added, the E. M. F. is given by

$$E_1 = E' - \frac{RT}{nF} \ln C_M, \text{ where } C_M = \text{total } Cd^{2+} \text{ ion concentration.}$$

When the ligand is added, some of the Cd^{2+} ions are removed to form a complex and the new potential would be set up. If this new E. M. F. is E_2, then

$$E_2 = E' - \frac{RT}{nF} \ln [M], \quad \text{where } [M] = \text{free } Cd^{2+} \text{ ion concentration.}$$

Hence,

$$\triangle E = E_2 - E_1 = \frac{RT}{nF} \ln \frac{C_M}{[M]}$$

$$= 0.03 \log_{10} \frac{C_M}{[M]}, \text{ at } 30^\circ.$$

TABLE I

Cadmium-pyridine system.

Conc. of Cd^{2+}=1.049 m*M*. Conc. of $NaClO_4$=0.1*M*.

[L] (m*M*).	ΔE (mV).	$\frac{C_M}{[M]}$.	F_1 (L).	F_2 (L).	F_3 (L).
50.15	10.0	2.154	23.01	100.00	199.40
98.85	17.6	2.860	28.93	110.56	207.98
161.99	25.8	6.244	38.54	126.81	227.22
233.42	32.8	11.400	48.84	132.10	180.36
309.40	39.3	19.420	62.76	144.68	176.73
392.93	46.0	33.140	84.34	168.84	200.65
487.09	51.4	50.680	104.05	176.65	177.89
588.24	57.0	78.430	133.33	196.06	180.30
686.44	61.6	112.100	163.30	211.68	177.26
792.25	66.8	167.500	211.42	244.14	194.56
882.99	70.6	224.600	254.36	267.68	201.22
961.66	73.3	276.500	287.52	280.27	197.85
			β_1=18	β_2=90	β_3=195

TABLE II

Cadmium—β-picoline system.

Conc. of Cd^{2+}= 1.049 m*M*. Conc. of $NaClO_4$=0.1*M*.

[L] (m*M*).	ΔE (mV).	$\frac{C_M}{[M]}$.	F_1 (L).	F_2 (L).	F_3 (L).
19.35	5.7	1.550	28.44	151.90	304.83
45.87	12.0	2.512	32.96	162.61	362.07
71.64	17.1	3.715	37.89	172.94	376.02
107.09	23.0	5.842	45.21	184.05	355.31
146.71	28.5	8.913	53.94	193.85	326.15
185.72	33.0	12.590	62.40	198.69	283.71
234.47	38.4	19.050	76.98	219.56	313.73
278.77	42.8	26.710	92.23	239.37	333.74
322.64	46.4	35.210	106.03	249.60	321.19
372.54	50.5	48.220	126.76	271.78	337.63
424.32	54.0	63.100	146.35	284.81	327.13
482.92	57.5	82.520	168.81	296.26	311.15
			β_1=25.5	β_2=146	β_3=345

TABLE III

Cadmium—γ-picoline system.

Conc. of Cd^{2+}=1.049 m*M*. Conc. of $NaClO_4$ =0.1*M*.

[L] (m*M*).	ΔE (mV).	$\frac{C_M}{[M]}$.	F_1 (L).	F_2 (L).	F_3 (L).
7.81	2.9	1.255	32.71	154.40	947.22
27.07	8.9	1.978	36.14	170.82	879.87
42.96	13.0	2.705	39.68	190.37	1009.50
60.80	16.9	3.650	43.58	198.72	850.24
83.36	21.6	5.220	50.63	229.47	989.32
110.99	26.5	7.614	59.59	253.09	955.85
145.25	32.0	11.600	72.97	285.54	953.79
191.13	38.6	19.230	95.38	334.20	979.41
242.62	44.5	30.230	120.47	366.73	905.65
282.05	49.3	43.650	151.21	424.45	983.70
326.82	53.5	60.230	181.23	458.15	952.06
379.53	58.0	85.020	221.38	500.30	930.89
			β_1=31.5	β_2=147	β_3=941

In Tables I to III are recorded the data obtained for the changes in E. M. F. with increasing concentration of ligand and consequent functions, calculated by the method suggested by Leden (*loc. cit.*), as follows:

$$F_1(\mathrm{L}) = \frac{\frac{C_M}{[M]} - 1}{[L]} = \beta_1 + \beta_2[\mathrm{L}] + \beta_3[\mathrm{L}]^2 \ldots + \beta_n[\mathrm{L}]^{n-1}$$

$$F_2(\mathrm{L}) = \frac{F_1(\mathrm{L}) - \beta_1}{[L]} = \beta_2 + \beta_3[\mathrm{L}] \ldots + \beta_n[\mathrm{L}]^{n-2}$$

$$F_3(\mathrm{L}) = \frac{F_2(\mathrm{L}) - \beta_2}{[L]} = \beta_3 + \ldots + \beta_n[\mathrm{L}]^{n-3}$$

$$F_n(\mathrm{L}) = \frac{F_{n-1}(\mathrm{L}) - \beta_{n-1}}{[L]} = \beta_n \ldots$$

where $\beta_n = K_1 . K_2 . K_3, \ldots K_n$, K_n being the stability constant of nth stage.

The consecutive overall formation constants β_n were obtained by the extrapolation of the plots of such functions against free ligand conc. $[L]$. A typical extrapolation is given in Fig. 1. β_3 values are taken from the average of $F_3(\mathrm{L})$. The free ligand concentration [L] was assumed to be the same as the total ligand concentration C_L, which is permissible in such weak complexes. In Table IV, the data evaluated for the stepwise stability constants K_n are surveyed.

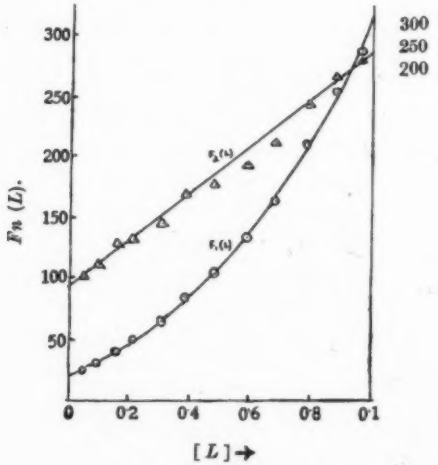

FIG. 1. Cd^{2+}—pyridine.

TABLE IV

Ligand.	pK_a.	Log K_1.	Log K_2.	Log K_3.	Log β_3.
Pyridine	5.17	1.26	0.70	0.34	2.29
β-Picoline	5.68	1.41	0.76	0.37	2.54
γ-Picoline	6.02	1.50	0.67	0.81	2.97

DISCUSSION

Data in Tables I to IV show that the complex formation takes place between Cd^{2+} ions and pyridine, β-picoline, and γ-picoline, the metal ion to ligand ratio being 1:1, 1:2, and 1:3. Although Bailar *et al.* (*loc. cit.*) reported the existence of 1:4 complex in Cd^{2+}—pyridine system, but under the conditions of the present investigation no evidence was obtained for such complex.

The values of the stability constants for Cd^{2+}—pyridine are observed to be in fair agreement with those obtained by Morinaga (*loc. cit.* Cf. $\beta_1=23$, $\beta_2=90$, and $\beta_3=187$). In the light of these observations the higher value of $\beta_3=574$, determined by Liu and Fu (*loc. cit.*), appears to be somewhat surprising.

Table IV points out that the stability constants of the different complexes lie in the ligand order: γ-picoline $>\beta$-picoline $>$ pyridine. This order compares very well with that of their pK_a values (Brown and Mihm, *J. Amer. Chem. Soc.*, 1955, **77**, 1723). Incidentally, the plot of log K_1 against pK_a was found to be a straight line (Fig. 2). The increase in the stability of picoline complexes can be attributed to the electron donating nature of the—CH_3 group which augments the corresponding electron-donating tendency of the heterocyclic nitrogen, the co-ordinating site of the ligands. The increased stability of β-picoline is due to the inductive effect of the-CH_3 group. In case of γ-picoline complexes, in addition to this inductive effect, there is also a mesomeric effect contributing towards their greater stability.

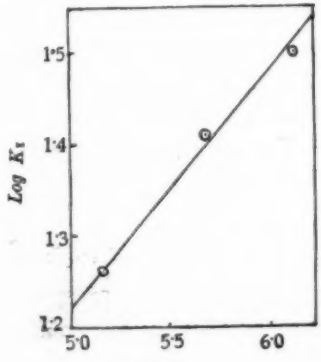

FIG. 2

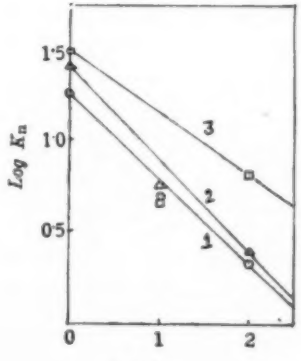

FIG. 3

1. Cd^{2+}—pyridine.
2. ,, —β-picoline.
3. ,, —γ-picoline.

A large number of data is available on the Ag^+—complexes of these ligands, the stabilities of which can be compared with those of the Cd^{2+}—complexes reported in this investigation. It is ordinarily expected that on account of the increased charge on the ion, Cd^{2+}—complexes may be more stable than their Ag^+ counterparts. The observation, however, is not in keeping with this expectation and can hardly be explained entirely on the basis of the difference between their ionic radii and the polarizing action of the central metal ions. Notwithstanding this, the following explanation may account for this observation.

Very recently, Yatsimirski ("Instability Constants of Complex Compounds", p. 69, Pergamon Press, 1960) and Irving ("The Stability of Metal Complexes", International Conference on Co-ordination Chemistry, London, April 6-11, 1959, p. 13, Chemical Society, London, Pub. No. 13) have pointed out that when dative π-bond is formed inside the complex particle between the ligand and the central atom, the exceptional behaviour as recorded above is noted. This happens because the strength of the π-bond decreases with increase in the charge of the central ion.

An attempt at the application of the empirical equation of Van Panthaleon and Van Eck (*Rec. trav. chim.*, 1953, **72**, 529) for the stepwise stability constants,

$$\log K_n = \log K_1 - 2\lambda(n-1)$$

(where 'λ' is constant and 'n', the number of attached ligands), to the present data did not meet with success. Fig. 3 shows that log K_2 values are lower than the requisite ones for them to lie on a straight line plot of log K_n against (n-1). This finding was then examined from another angle. The change in the magnitude of stepwise constants with the change in the number of ligands is also determined by the stereochemical characteristics of the compounds concerned. Cd^{2+} ion is generally known to form a tetrahedral structure with complexing ligands as there is no vacant d-orbital for the formation of planar or octahedral configuration. Viewed from this point, one is struck with the fact that a dipole-dipole interaction would occur between the ligands in the species ML_2 when they are situated at the apices of a tetrahedron. This may give rise to a sort of repulsive effect which would operate to a greater extent in a tetrahedral than in a planar or octahedral structure, thereby decreasing the second stability constant. This observation is in agreement with that of Yatsimirski (*loc. cit.*) in the case of tetrahedral co-ordination.

The similar studies with α-picoline show that the complex formed must have been very weak, as the cadmium hydroxide is invariably found to precipitate owing to hydrolysis, which predominates here over complex formation. This behaviour is distinctly different from that of Ag^+—complexes of α-picoline, the stability of which is of the same order of corresponding Ag^+—complexes of β- and γ-picolines. The probable explanation is that in α position a sufficiently large $-CH_3$ group offers a steric hindrance to Cd^{2+} ion for the formation of the possible tetrahedral complex. In case of Ag^+—complex of α-picoline, such a possibility cannot exist as the structure would be linear.

Grateful acknowledgements are due to the Ministry of Scientific Research and Cultural Affairs, Govt. of India, for the award of a senior research scholarship to one of the authors (A. G. Desai).

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A Quantitative Study of Oxidation Products of Iodine at the End Points of the Titrations of Mercuric and Silver Salts with Iodine-Iodide Solutions

Kshitish Chandra Seal

A quantitative study of a reaction mechanism in the tritration of mercuric or silver salts with iodine-iodide solution under certain conditions has been made, which shows that iodine is oxidised to hypoiodous acid and iodate.

Seal (this *Journal*, 1958, **35**, 453; *Ind. & News Ed.*, 1955, **18**, 209) titrated mercuric chloride with iodine-iodide solution in presence of an excess of $NaHCO_3$ and titrated silver with iodine-iodide solution in sodium acetate buffer medium and developed empirical methods of estimating mercury and silver respectively. The present paper describes the mechanism of apparently complicated reactions of iodine-iodide solution with mercuric or silver salts in the titration.

In presence of $NaHCO_3$ or in sodium acetate buffer medium, mercuric or silver ions react with iodine with the formation of unstable hypoiodous acid:

$$\overset{+}{M}eq + I_2 + H_2O \equiv MeqI + HIO + H^+ \quad .. \quad .. \quad (1)$$

But the HIO being unstable decomposes to HIO_3 and the regenerated HI further reacts with mercuric or silver ions:

$$\begin{aligned} 3\overset{+}{M}eq + 3I_2 + 3H_2O &= 3HIO + 3MeqI + 3H^+ \\ 3HIO &= HIO_3 + 2HI \quad .. \quad .. \quad (2) \\ 2\overset{+}{M}eq + 2HI &= 2MeqI + 2H^+ \end{aligned}$$

$$5\overset{+}{M}eq + 3I_2 + 3H_2O = 5MeqI + HIO_3 + 5H^+ \quad .. \quad (3)$$

Note 1: $\overset{+}{M}eq = Ag^+$ or $1/2\ Hg^{2+}$.

Note 2: Actually HIO_3 is present as $NaIO_3$ in presence of $NaHCO_3$ or sodium acetate and an equivalent proportion of CO_2 or acetic acid is liberated.

The reaction of mercuric or silver ions with KI is simple:

$$\overset{+}{M}eq + KI = MeqI + K^+ \quad (4)$$

Now, experiments reveal that all the hypoiodous acid formed does not completely decompose as shown in reaction (2). At the end point, when all the mercuric or silver ions are precipitated as iodide, a small amount of hypoiodous acid still remains undecomposed. This is decomposed by the KI added during the second titration after the first end point:

$$IO^- + I^- + H_2O = I_2 + 2OH^- \quad .. \quad .. \quad (5)$$

In presence of an excess of $NaHCO_3$ or sodium acetate the alkalinity is so repressed that

this reaction proceeds quantitatively to right hand. The determination of the liberated iodine gives the amount of undecomposed hypoiodous acid. The mercury or silver equivalent to this HIO can be calculated stoichiometrically from equation (1).

After the estimation of HIO, the solution is acidified with hydrochloric acid when fresh iodine is liberated by the decomposition of $NaIO_3$:

$$NaIO_3+5KI+6HCl = 3I_2+5KCl+NaCl+3H_2O \quad .. \quad (6)$$

The amount of $NaIO_3$ is estimated by titrating this iodine. The mercury or silver equivalent to $NaIO_3$ is calculated stoichiometrically from equation (3).

In presence of $NaHCO_3$, iodate cannot be estimated quantitatively as CO_2 carries with it a portion of iodine. But it can be estimated in presence of sodium acetate. When $NaHCO_3$ is used, the amount of $NaIO_3$ formed is calculated indirectly by deducting the iodine liberated by HIO from the total iodine consumed in the titration of mercuric or silver ions.

As a known amount of KI is taken in the reagent solution, the mercury or silver equivalent to it can be calculated from equation (4).

EXPERIMENTAL

Mercuric chloride solutions were prepared by weighing chemically pure salt (the purity checked by the standard gravimetric method) and dissolving in water. Mercuric nitrate, sulphate, and acetate solutions were obtained by dissolving pure mercuric oxide (the purity checked by the thiocyanate method) respectively in the requisite amount of nitric, sulphuric, and acetic acid and diluting with water. Silver solution was prepared by weighing silver nitrate (A.R.) and dissolving it in water.

Potassium iodide of Merck's G. R. quality (the purity checked by Volhard's method), sodium acetate of B. D. H. pure quality, and $NaHCO_3$ of Merck's extra pure quality were used.

Determination of IO^- *and* IO_3^- *at the End Point of Titration of* $HgCl_2$ *with* KI—I_2 *Solution and Calculation of* Hg *therefrom*

(*a*) *When Sodium Acetate Buffer is used.*—(*i*). To a neutral mercuric chloride solution (8 to 25 mg. Hg in 75 c.c.), taken in a 250 c.c. conical flask, a 20% sodium acetate solution (25 c.c.) was added. The solution was titrated with *N*/50 iodine (KI content 4.0g./litre) as usual to the first definite strach-iodide end point. Immediately, potassium iodide (0.5 g. approx.) was added and the liberated iodine was titrated with a standard *N*/50 sodium thiosulphate solution. When the starch-iodide colour just disappeared, HCl (conc., 5-6 c.c. approx.) was added and the freshly liberated iodine was titrated with *N*/50 thiosulphate. The amounts of HIO and $NaIO_3$ were calculated from the volumes of thiosulphate solution.

(*ii*). To a mercuric chloride solution (20 to 150 mg. Hg in 150 c.c.) a 20% sodium acetate solution (50 c.c.) was added. For titrations *N*/20 iodine (KI content 10.0 g. per litre) and *N*/20 thiosulphate solution were used. HCl (conc., 10 c.c.) was added for liberation of iodine by iodate.

The results are shown in Table I along with the stoichiometrically calculated values of mercury.

TABLE I

Amounts of HIO *and* $NaIO_3$ *and their Hg equivalent when*

TABLE I

Amounts of HIO *and* $NaIO_3$ *and their* Hg *equivalent* when Na *acetate buffer was used.*

1 Meq. of iodine (converted to HIO $\equiv 0.0502 \times 10^3$ mg. Hg. 1 Meq. of iodine (converted to HIO_3) $\equiv 0.0836 \times 10^3$ mg. Hg. 1 Mg. of KI $\equiv 0.60422$ mg. Hg.

Sl. No.	Hg. present.	Reagent solutions. Iodine.	KI.	Iodine equiv. of HIO.	$NaIO_3$.	Hg equivalents of HIO.	$NaIO_3$.	KI.	Total Hg found.
1.	8.8053 mg.	0.04752 meq.	9.5424 mg.	0.02988 meq.	0.01792 meq.	1.500 mg.	1.498 mg	5.766 mg.	8.764 mg.
2.	11.0066	0.05842	11.7292	0.03386	0.02590	1.700	2.165	7.087	10.952
3.	44.0263	0.22430	45.9730	0.08375	0.13790	4.204	11.528	27.778	43.510
4.	55.0330	0.27405	56.1610	0.08375	0.19085	4.204	15.955	33.934	54.093
5.	110.0660	0.55050	112.8190	0.11330	0.43710	5.688	36.542	68.167	110.397
6.	154.0920	0.76145	156.0580	0.11575	0.64395	5.811	53.834	94.293	153.938

TABLE II

Amounts of HIO *and their* Hg *equiv. when* $NaHCO_3$ *was used.*

Sl. No.	Hg Calc.	Reagent solutions. Iodine.	KI	Iodine equiv. of HIO.	Hg equivalents of HIO.	$NaIO_3$.	KI.	Total Hg found.
				Mercuric chloride.				
1.	44.026 mg.	0.22540 meq.	45.172 mg.	0.0500 meq.	2.510 mg.	14.663 mg.	27.294 mg.	44.467 mg.
2.	55.033	0.28175	56.465	0.0625	3.138	18.329	34.117	55.584
3.	110.066	0.54390	109.002	0.0450	2.259	41.708	65.861	109.828
				Mercuric nitrate.				
1.	54.903	0.27760	56.658	0.0500	2.510	19.027	34.234	55.771
2.	68.629	0.34335	70.077	0.0625	3.138	23.479	42.342	68.959
3.	137.259	0.67695	138.166	0.0675	3.389	50.950	83.483	137.822
				Mercuric sulphate.				
1.	54.903	0.28003	57.155	0.0875	4.393	16.097	34.534	55.024
2.	68.629	0.34090	69.580	0.0550	2.761	23.901	42.042	68.704
3.	137.259	0.66475	135.681	0.0575	2.887	50.766	81.981	135.634
				Mercuric acetate.				
1.	54.903	0.28245	57.652	0.0750	3.765	17.343	34.835	55.943
2.	68.629	0.34090	69.580	0.0700	3.514	22.647	42.042	68.203
3.	137.259	0.67085	136.924	0.0700	3.514	50.231	82.732	136.477

TABLE III

Amounts of HIO *and* $NaIO_3$ *and their* Ag *equiv. when* Na *acetate buffer was used.*
1 Meq of iodine (converted to HIO) $\equiv 0.540 \times 10^3$ mg. Ag. 1 Meq of iodine (converted to HIO_3) $\equiv 0.0900 \times 10^3$ mg. Ag. 1 Mg. of KI $\equiv 0.6506$ mg. Ag.

Sl. No.	Ag present.	Reagent solutions. Iodine.	KI.	Iodine equivalents of HIO.	$NaIO_3$.	Ag equivalents of HIO.	$NaIO_3$.	KI.	Total Ag found.
1.	4.320 mg.	0.02163 meq.	4.43324 mg.	0.01346 meq.	0.00743 meq.	0.727 mg.	0.669 mg.	2.884 mg.	4.280 mg.
2.	5.400	0.02755	5.64592	0.01841	0.00817	0.994	0.735	3.673	5.402
3.	7.560	0.03841	7.87248	0.02287	0.01485	1.235	1.337	5.122	7.694
4.	8.640	0.04132	8.46888	0.02584	0.01609	1.395	1.448	5.510	8.353
5.	10.800	0.05151	10.55628	0.02861	0.02450	1.545	2.205	6.868	10.618
6.	16.200	0.07760	15.9040	0.04474	0.03604	2.416	3.244	10.347	16.007
7.	27.000	0.12852	26.3410	0.05464	0.07672	2.951	6.905	17.137	26.993
8.	54.000	0.24930	51.0916	0.06158	0.19206	3.325	17.285	33.240	53.850

TABLE IV

Amounts of HIO *and their* Ag *equiv. when* $NaHCO_3$ *was used.*

Sl. No.	Ag. Present.	Reagent solutions. Iodine.	KI	Iodine equiv. of HIO.	Ag equivalents of HIO.	$NaIO_3$.	KI.	Total Ag found.
1.	10.800 mg.	0.04948 meq.	10.1388 mg.	0.01900 meq.	1.026 mg.	2.743 mg.	6.596 mg.	10.365 mg.
2.	21.600	0.09992	20.4764	0.02574	1.390	6.676	13.322	21.388
3.	27.000	0.12222	25.0488	0.02674	1.444	8.593	16.297	26.334
4.	43.200	0.19430	39.7600	0.02178	1.176	15.500	25.868	42.544
5.	54.000	0.24348	49.8988	0.02906	1.569	19.298	32.464	53.331
6.	75.600	0.33854	69.3812	0.02812	1.518	27.938	45.139	74.595

(*b*) *When* $NaHCO_3$ *buffer is used.*—Immediately after the end point of the titration of mercuric salt solution in presence of an excess of $NaHCO_3$ with iodine-iodide solution, KI was added and the liberated iodine was titrated with a standard sodium arsenite solution as usual. The iodate equivalent of iodine was then found out by deducting the HIO equivalent of iodine from the total amount of iodine added in the original titration of Hg.

When $Hg(NO_3)_2$ and $HgSO_4$ solutions were titrated, sodium chloride (pure, 0.05-0.1 g) was added before the addition of $NaHCO_3$ or Na acetate. The results are shown in Table II.

Determination of IO^- *and* IO_3^- *at the End Point of Titration of* $AgNO_3$ *Solution with* KI-I_2 Solution *and Caiculation of Silver therefrom*

(*c*) *When Sodium Acetate Buffer is used.*—To a neutral silver nitrate solution (4.0—10 mg. Ag in 25 c.c.) a 10% sodium acetate solution (25 c.c.) was added and the experiment was carried out as described in clause *a*(*i*) using standard solutions of strength *N*/100 instead of *N*/50. For solutions containing 10-50 mg. Ag in 75 c.c., experiment was done as described in clause *a* (*i*). The results are shown in Table III along with the stoichiometrically calculated values of Ag.

(*d*) *When* $NaHCO_3$ *Buffer is used.*—To the neutral solution of Ag. (10-75 mg. in 100c.c.) sodium bicarbonate (1-2 g. approx.) instead of sodium acetate was added before titration with iodine-iodide solution and the estimation of HIO was made as usual. The iodate equivalent of iodine was found out by deducting the HIO equivalent of iodine from the amount of iodine originally required in the titration of Ag solution. The results are shown in Table IV.

Effect of the Time taken for Titration

It was observed in duplicate titrations of Hg by the empirical method that the volumes of iodine-iodide solution varied by 2-3 drops depending on the time taken for titration. The reason seems to be that during titration hypoiodous acid formed suffers decomposition and longer is the time taken for titration, greater is the decomposition. The time effect on the titration of mercuric chloride solution in presence of $NaHCO_3$ is recorded in Table V.

TABLE V

Hg (in 200 c.c.) = 110.066 mg.

Sl. No.	Iodine-iodide solution.	Time taken for titration.	As_2O_3 soln. (*N*/20) equiv. to HIO (formed).
1.	10.947 c.c.	50 sec.	1.50 c.c.
2.	10.898	60	1.40
3.	10.824	124	1.00
4.	10.799	157	0.925
5.	10.775	204	0.725
6.	10.750	281	0.725

DISCUSSION

At lower concentrations of the metals, the amounts of HIO formed is more than the amounts of $NaIO_3$; but as their concentrations rise, the amounts of $NaIO_3$ are observed more than that of HIO. Evidently $NaIO_3$ is the decomposition product of HIO.

The reaction mechanism is not changed appreciably in presence of nitrates, sulphates, phosphates, acetates, citrates, and a small amount of chlorides. In presence of $NaHCO_3$, the chloride content as NaCl should preferably be below 0.25 g./100 c.c. of the test solution and in sodium acetate buffer, it should not be more than that equivalent to Hg. The *p*H of the test solution is maintained between 7.2 and 8.5 approximately both for mercury and silver. Free CO_2 sometimes brings down the *p*H of the sodium acetate solution to below 7; it is not desirable when acetate buffer is used for Hg. Hence for an accurate result of Hg in the empirical direct titrimetric method, chlorides, free CO_2, and the *p*H should be controlled in the test solution as well as in the standardisation. For better end point in the majority of cases, $NaHCO_3$ is preferable to sodium acetate buffer in the case of Hg. As shown in Tables III and IV, better recovery of Ag is observed with sodium acetate buffer than with $NaHCO_3$.

Sometimes, on the addition of $NaHCO_3$ or sodium acetate to the solutions of mercuric compounds, especially nitrate, sulphate, etc., the precipitation of yellow or yellowish red mercury compounds was observed in which case the titration became very slow at a later stage. To overcome this, a small amount of sodium chloride (0.05—0.1g) was added to the test solution. It is also desirable to dilute the test solution of mercuric salt as far as practicable with water before the addition of $NaHCO_3$ or sodium acetate.

In the empirical method for the evaluation of Hg, the time taken for titration of the test solution and for standardisation should practically be the same, preferably 3 to 4 mins. (cf. Table V).

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Clay Membrane Electrode as a Tool for Cationic Activity Measurement in Solution

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Attempts have been made to prepare clay membrane electrodes suitable for measurement of cationic activities in solutions from some of the Indian clays. Padegaon soil clay (montmorillonite) membrane in its Ca-form performs best in comparison to the other clay membranes, e.g., Chinsura soil clay (montmorillonite), Contai soil clay (illite), etc. The membranes prepared from a kaolinite clay did not at all respond as an electrode. Padegaon soil clay contains free oxides, e.g., of iron and aluminium, but it is superior to 'pure' montmorillonite clay, e.g., aquagel, and also to a vermiculite having a higher b.e.c., so far as the performance of the membranes prepared from these clays is concerned. The removal of free oxides impairs the physical condition of the membranes, but their electrochemical performance is more or less maintained. Small additions of hydroxide sols of iron and aluminium to the cleaned clay suspensions improve neither the physical condition of the membranes prepared from them, nor their electrochemical performance. On the other hand, in some cases such membranes lose their responsiveness to electrochemical measurements.

The use of clay membrane electrodes for the measurements of cationic activity was first demonstrated by Marshall (*J. Phys. Chem.*, 1939, **43**, 1158), who also worked out the conditions and limitations of the measurements (*ibid.*, 1948, **52**, 1284) and the interpretations of experimental data in the light of the existing theories of Teorell (*Proc. Soc. Exptl. Biol. Med.*, 1935, **33**, 282) and Meyer and Sievers (*Helv. Chim. Acta*, 1936, **19**, 649). The experimental work has been extended to the measurements of activities of a large number of mono- and bivalent cations by Marshall *et al.* (*loc. cit.*), Mitra and Chatterjee (*J. Indian Soc. Soil Sci.*, 1953, **1**, 12), Bose (this *Journal*, 1960, **37**, 465) and Adhikari (*J. Indian Soc. Soil Sci.*, 1957, **5**, 198; *Indian J. Appl. Chem.*, 1958, **21**, 149). The action of the clay membranes as reversible electrodes being dependent on the exchangeability of the cations on the surface, a high base-exchange capacity is desirable, for which montmorillonite and beidellite clays have been mostly used. Since the cations differ in their exchangeability, often quite markedly, the ranges of their activity registered by membrane electrodes will certainly be different. In fact, the ranges of validity of the Nernst equation, attainment of equilibrium with outside ions, and other electrochemical performances of the same membranes vary appreciably with cations. About the use of different clay minerals as materials for membrane electrodes, very little is known. The studies by Mitra (D. Phil. thesis, Calcutta University, 1954) and Bose (*loc. cit.*) have shown that among others Padegaon clay, which is predominantly montmorillonitic and contains considerable amounts of free sesquioxides of iron and aluminium, performs quite satisfactorily as membrane electrode material. It is, however, not known whether these free oxides play any role in so far as the electrochemical behaviour of membrane electrodes is concerned. The object of the present paper is to investigate this aspect of the problem.

EXPERIMENTAL

Clay fractions ($<0.5\mu$) were isolated from Padegaon soil (montmorillonite), aquagel (montmorillonite), Chinsura soil clay (montmorillonite with a trace of kaolinite), Contai

soil clay (illite), Bagespura vermiculite (vermiculite), and Rajmahal kaolinite (kaolinite). The sesquioxides were removed from the clays following the procedure of Marshall and Jeffries (*Soil Sci. Soc. Am. Proc.*, 1945, **10**, 397). The original clays as well as the oxide-free samples were electrodialysed in order to prepare hydrogen clays; Ca-form and Na-form were prepared by treatment with requisite amounts of calcium oxide and NaOH. The clay membranes were prepared as usual by slow evaporation at 70-80° of 1.5—2% suspension under an infrared lamp. These were then cut into small discs and heated for 48 hours at 590-600°. Membranes were similarly prepared from 1 to 0.5μ size fractions of Chinsura soil clay and Bagespura vermiculite, and also from the $<2\mu$ fraction of Bagespura clay. The usual procedure of measuring the cation activities with membranes as prepared was followed (vide Mitra, *loc. cit.*).

The results of such measurements with membrane electrodes, prepared from different clays, are recorded in Table I-V, in which together with the range of applicability of Nernst equation, the electrical resistance, thickness, and composition of these membranes are shown.

DISCUSSION

The electrical resistances per mm of the membranes having the same cross section are small for those prepared from soil clays when compared with those from 'pure' clay minerals. Membranes prepared from the illitic clay from Contai soil possess comparatively low electrical resistance. Those containing relatively coarse fractions of clay are somewhat better for activity measurements. At the same time their electrical resistance is lowered and physical conditions remain unimpaired. The electrical resistance of the membranes depends on the cation saturating the clay and increases in the order: Ca-form < H-form <Na-form. The removal of free oxides from soil clays does not appreciably alter the electrical resistance, but makes the membranes prepared from them brittle. Moreover, the surface curls up on drying and often cracks, and hence it is difficult to bring them into suitable form for measurement.

Referring to Table I, the range of obedience to the Nernst equation is greater with the Padegaon Ca-form and aquagel Ca-or Na-form membranes for NH_4^+ and K^+ ions, the range of activities being 0.0001 to 0.01 for NH_4^+ and 0.00011 to 0.243 for K^+; with the other membranes the range of activities measureable is much less. For Na^+, Ca^{2+}, Mg^{2+}, Ba^{2+}, the range of activities, measureable within one tenth of a millivolt, is greatest with the Padegaon Ca- and Na-forms of membrane, the ranges being 0.00097 to 0.2367 for Na^+, 0.0001 to 0.0243 for both Ca^{2+} and Mg^{2+}, and 0.0001 to 0.0081 for Ba^{2+}. With the other membranes the measureable range is small.

In order to find out the influence, if any, of free oxides present in the soil clays on membrane performance, membranes were prepared from these soil clays after careful removal of free oxides according to the method of Marshall and Jeffries (*loc. cit.*). Unfortunately, however, the membranes of cleaned clays cracked and curled up on the surface on drying in the usual manner, viz., at 70-80°. Evaporation at 50-60° enabled us to get the membranes without much cracking and curling, but these were mechanically less strong than the original ones. The measurements made with some of these membranes, which are recorded in Table II, show that the oxide-free membranes have more or less maintained their electrochemical performance. The same remarks apply to the illitic Contai clay membranes, which were studied in a similar manner.

TABLE I

TABLE I

Materials of membrane.	B.e.c. (me/100g. of clay).	Resistance in ohm/mm thickness.	Thickness of the film (mm).	Range of obedience to the Nernst equation. $a_{NH_4}^{+}$.	a_K^{+}.	a_{Na}^{+}.	a_{Ca}^{2+}.	a_{Mg}^{2+}.	a_{Ba}^{2+}.
Padegaon, original	81	1240	0.25	0.0001-0.001	0.00011-0.081	0.00097-0.0789	0.0001-0.0081	0.0001-0.0081	—
0.5μsize H-form									
„ Na-form		4666	0.30	0.0001-0.001	0.00011-0.243	.00097-0.2367	.0001-0.0243	0.0001-0.0243	0.0001-0.0081
„ Ca-form		1033	0.30	0.0001-0.01	„	„	„	„	„
Contai, original									
0.5μsize, H-form	52	566	0.30	0.0001-0.001	0.00011-0.009	0.00097-0.0087	0.0001-0.0009	0.0001-0.0009	—
„ Na-from		1500	0.30	„	„	0.00097-0.0263	0.0001-0.0027	0.0001-0.0027	0.0001-0.0009
„ Ca-form		400	0.25	„	„	„	„	„	„
Chinsura, original									
0.5μsize, H-form	74.5	1000	0.20	0.0001-0.001	0.00011-0.0027	0.00097-.0263	0.0001-0.0009	—	—
„ Na-form		1110	0.27	„	„	„	0.0001-0.0027	0.0001-0.009	—
„ Ca-form		1900	0.25	„	„	.00097-.0789	0.001-0.0081	0.0001-0.0087	0.0001-0.0081
Aquagel									
0.5μsize, H-form	113	1500	0.25	0.0001-0.01	0.00011-0.081	0.00097-0.0789	0.0001-0.0081	0.0001-0.0081	0.0001-0.0081
„ Na-form		9000	0.25	„	0.00011-0.243	„	„	„	„
„ Ca-form		1200	0.25	„	„	„	„	„	„

TABLE II

Materials of membrane.	B.e.c. (m.e./100g. of clay).	Resistance in ohm/mm thickness.	Thickness (mm).	Range of obedience to the Nernst equation. $a_{NH_4}^{+}$.	a_K^{+}.	a_{Na}^{+}.	a_{Ca}^{2+}.	a_{Mg}^{2+}.	a_{Ba}^{2+}.
Padegaon, oxide-free									
0.5μsize, H-form.	90	1200	0.50	0.0001-0.001	0.00011-0.081	0.00097-0.0289	0.0001-0.0081	0.0001-0.0081	
„ Na-form		4800	0.25	0.0001-0.01	0.00011-0.241	0.00097-0.2367	0.0001-0.0243	0.0001-0.0081	0.0001-0.0081
„ Ca-form		1240	0.25	0.0001-0.01	0.00011-0.241	0.00097-0.2367	0.0001-0.0243	0.0001-0.0081	0.0001-0.0081
Contai, oxide-free									
0.5μsize, H-form.	54	500	0.20	0.0001-0.001	0.00011-0.027	0.00097-0.00877	0.001-0.0027	0.0001-0.009	—
„ Na-form		650	0.20	„	0.00011-0.009	0.00097-0.0263	„	„	„
„ Ca-form		400	0.25	„	„	„	„	„	„
Chinsura, oxide-free									
0.5μsize, H-form	70	800	0.30	0.0001-0.001	0.0001-0.027	0.00097-0.0263	0.0001-0.0027	0.0001-0.0009	—
„ Na-form		1000	0.25	„	„	0.00097-0.0789	„	0.0001-0.0081	0.0001-0.0027
„ Ca-form		700	0.25	„	„	„	0.0001-0.0081	„	0.0001-0.0081

TABLE III

Materials of membrane.	B.e.c. (m.e./100g. clay).	Resistance in ohm/mm thickness.	Thickness (mm).	Range of obedience to the Nernst equation. $a_{NH_4^+}$.	a_{K^+}.	a_{Na^+}.	$a_{Ca^{2+}}$.	$a_{Mg^{2+}}$.	$a_{Ba^{2+}}$.
Bagespura, original									
0.5μsize, H-form	118	2400	0.23	0.0001-0.001	0.00011-0.081	0.00097-0.0263	0.0001-0.0009	0.0001-0.00081	0.0001-0.0009
,, Na-form		2600	0.20	,,	,,	,,	,,	,,	,,
Bagespura, oxide-free									
0.5μsize, H-form	100	2500	0.25	,,	,,	,,	,,	,,	,,
,, Na-form		2800	0.25	,,	,,	,,	,,	,,	,,
Rajmahal kaolinite									
0.5μsize, H-form	6.5	..	..	..	..	..	..	..	..
,, Na-form		500	0.25	Nil	Nil	Nil	..	..	..
,, Ca-form		500	0.25	Nil	Nil	Nil	..	..	..

TABLE IV

Materials of membrane.	B.e.c. (m.e./100 g. clay).	Resistance in ohm/mm thickness.	Thickness (mm).	Range of obedience to the Nernst equation. $a_{NH_4^+}$.	a_{K^+}.	a_{Na^+}.	$a_{Ca^{2+}}$.	$a_{Mg^{2+}}$.	$a_{Ba^{2+}}$.
Chinsura, original									
1-0.5μsize, H-form	30	540	0.45	Nil	0.00011-0.0033	Nil	Nil	Nil	..
,, Na-form		450	0.33	,,	0.00011-0.009	0.00097-0.00292	0.001-0.0003	0.0001-0.0003	..
,, Ca-form		450	0.33	,,	,,	,,	,,	,,	..
Bagespura, original									
1-0.5μsize, H-form	114	2200	0.25	0.0001-0.001	0.00011-0.081	0.00097-0.0263	0.0001-0.0003	0.0001-0.0027	0.0001-0.0003
,, Na-form		2400	0.26	,,	,,	,,	,,	,,	,,
Bagespura, oxide-free									
1-0.5μsize, H-form	100	2400	0.25	,,	0.00011-0.081	,,	,,	,,	,,
,, Na-form		2560	0.33	,,	,,	,,	,,	,,	,,
Bagespura, original									
2μsize, H-form	108	2300	0.20	—	0.00011-0.009	0.00097-0.00877	,,	0.0001-0.0003	..
,, Na-form		2300	0.25	—	,,	,,	,,	,,	..
Bagespura, oxide-free									
2μsize, H-form	100	2160	0.24	—	,,	,,	,,	,,	..
,, Na-form		2265	0.33	—	,,	,,	,,	,,	..

TABLE V

Materials of membrane.	Resistance per mm. thickness.	Thickness (mm).	Range of obedience to the Nernst equation. $a_{NH_4^+}$.	a_{K^+}.	a_{Na^+}.	$a_{Ca^{2+}}$.
Chinsurah, oxide-free 0.5μ size+5% Al sol.	870	0.27	0.0001-0.001	0.00011-0.00033	0.00097-0.00292	0.0001-0.0009
Chinsurah, oxide-free 1-0.5μ size+5% Al sol	500	0.30	Nil	Nil	Nil	Nil
Bagespura, oxide-free 0.5μ size+5%Al sol	1550	0.20	0.00011-0.001	0.00011-0.001	0.00097-0.00292	0.0001-0.0009
Bagespura, oxide-free 1-0.5μ size+5% Al sol	1560	0.25	Nil	,,	,,	0.0001-0.0003
Padegaon, oxide-free 0.5μ size+5% $Fe(OH)_3$ sol	960	0.24	0.00011-0.001	0.00011-0.027	0.00097-0.0789	0.0001-0.0081
Contai, oxide-free 0.5μ size+5% $Fe(OH)_3$ sol	500	0.22	,,	0.00011-0.001	0.00097-0.0087	0.0001-0.0009
Aquagel+5% $Fe(OH)_3$ sol	840	0.37	,,	0.00011-0.027	,,	0.0001-0.0081

Bagespura vermiculite has a high b.e.c. and membranes of good quality have been prepared out of it. Referring to Table III, it is to be seen that in comparison to the Padegaon clay membranes, the range of obedience to the Nernst equation shown by the vermiculite membranes, both in H- and Ca-forms, is smaller, being approximately 0.0001 to 0.001 for NH_4^+, 0.00011 to 0.081 for K^+, 0.00097 to 0.0263 for Na^+, 0.0001 to 0.0009 for Ca^{2+} and Ba^{2+}, and 0.0001 to 0.00081 for Mg^{2+}. Taking these along with the results of the other montmorillonitic clay membranes, it might be said that a high exchange capacity of the material does not ensure better performance of the membranes prepared from them.

The effect of the size of the clay particle on the quality of the membranes can be seen from the data recorded in Table IV. Comparing these with the corresponding data in Table I, it is noticed that the performance of the membranes prepared from the larger size fractions of the clays does not improve, but in some cases, e.g., the Chinsura 1 to 0.05μ fractions, the range of performance is lowered.

Removal of the oxides has been shown to impair the physical condition of the membranes, but their electrochemical performance is more or less maintained. Some experiments were also done in order to find out if addition of sesquioxides in colloidal form to the cleaned clay suspensions, prior to membrane preparations, improved the physical quality or otherwise influence the membrane performance. Table V shows some of the results which demonstrate that the presence of free oxides in the form of added impurities reduces the range of performance of otherwise good membranes. The membranes of the 1-0.5μ size fractions, e.g., Chinsura (montmorillonite) and Bagespura (vermiculite), however, become altogether unresponsive as a result of addition of 5% by weight of an alumina sol.

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Chalkones. Part V. Synthesis of Hydroxy- and Methoxy-Chalkones and their Derivatives

Durga Nath Dhar*

Syntheses of some new hydroxy- and methoxy-chalkones by the Claisen-Schmidt condensation have been effected. The functional derivatives of some of the chalkones have been prepared.

In continuation of the previous work on chalkones (Dhar and Lal, *J. Org. Chem.*, 1958, **23**, 1159; Dhar, *ibid.*, 1960, **25**, 1247, this *Journal*, 1960, **37**, 320, 363, 496, 799; *J. Sci. Res., Agra Univ.*, 1961, **10**), the present communication reports the synthesis of some hydroxy- and methoxy-chalkones and their derivatives, viz., acetyl, benzyloxy, and 2,4-dinitrophenylhydrazone.

EXPERIMENTAL

The chalkones were prepared as described by Schraufstatter and Deutsch (*Ber.*, 1948, **81**, 489). The acetyl, benzyloxy, and 2, 4-dinitrophenylhydrazone derivatives were prepared according to the standard procedures.

TABLE I

Chalkone.	Colour & cryst. shape.	Cryst. from.	M.P.	Formula.	Found.	Calc.
2,3-Dimethoxy-2′-hydroxy-	Yellow needles	Ethanol	99-100°	$C_{17}H_{16}O_4$	C: 71.7% H: 5.4	71.8% 5.6
2,2′-Dihydroxy--3-methoxy-	,,	,,	151-52°	$C_{16}H_{14}O_4$	C: 71.0 H: 5.2	71.1 5.2
2′-Hydroxy-4-methoxy-	Stellate aggregate of yellow needles	,,	91-92°	$C_{16}H_{14}O_3$	C: 75.4 H: 5.6	75.6 5.5
2′,3-Dihydroxy-	Golden yellow prismatic needles	Aqueous ethanol	161°	$C_{15}H_{12}O_3$	C: 75.1 H: 4.9	75.0 5.0

TABLE II

Chalkone (derivative).	Colour & cryst. Shape.	Cryst. form.	M.P.	Formula.	Found.	Calc.
2-Acetoxy-2′,3,4′-trimethoxy-	Pale yellow, elongated prisms & hexagonal plates	95% Ethanol	90-91°	$C_{20}H_{20}O_6$	C: 66.7 H: 5.5	67.4 5.6
2-Acetoxy-2′,4′,6-trimethoxy-	Dull apple-green crystals	Ethanol	88-89°	$C_{20}H_{20}O_6$	C: 67.4 H: 5.4	67.4 5.6
3-Methoxy-2,2′,4′-triacetoxy-	Pale yellow prisms	Ether-pet. ether	93-94°	$C_{22}H_{20}O_8$	C: 64.0 H: 4.8	64.1 4.8
2′,4′,3-Triacetoxy-	Pale yellow biconvex plates	Ethanol	99-100°	$C_{21}H_{18}O_7$	C: 66.2 H: 4.7	65.9 4.7
3,4′-Dibenzyloxy-2′-hydroxy-	Yellow microneedles	Benzene-ethanol	134-35°	$C_{29}H_{24}O_4$	C: 79.8 H: 5.4	79.8 5.5.

2-Benzyloxy-2′,3,4′-trimethoxychalkone separated as a yellow oil, which failed to crystallise.

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TABLE III

Chalkone 2,4-D.N.P.	Colour and crystalline shape.	Cryst. from.	M.P.	Formula.	%Nitrogen. Found.	Calc.
2,3-Dimethoxy-2′-hydroxy-	Red microneedles	Ethanol	220-21°	$C_{23}H_{20}O_7N_4$	11.9	12.1
2,2′-Dihydroxy-3-methoxy-	,,	,,	237-38°	$C_{22}H_{18}O_7N_4$	12.6	12.4
2′-Hydroxy-4-methoxy-	Orange, hair-like needles	Xylene	254°	$C_{22}H_{18}O_6N_4$	12.8	12.9
2-Hydroxy-2′,3,4′-trimethoxy-	Bright red, rod-like microcrystals	Ethyl acetate	222°	$C_{24}H_{22}O_8N_4$	11.4	11.3
2-Benzyolxy-2′3,4′-trimethoxy-	Deep orange-red needles	,,	193-94°	$C_{31}H_{28}O_8N_4$	9.8	9.6
2-Hydroxy-2′,4′,6′-trimethoxy-	Vermilion rod-type microneedles	Ethanol-acetone	220-21°	$C_{24}H_{22}O_8N_4$	11.5	11.3
3-Methoxy-2,2′,4′-trihydroxy-	Deep red microneedles	Ethyl acetate	207-208°	$C_{22}H_{18}O_8N_4$	11.9	12.0
2′,3-Dihydroxy-	Bright red microneedles	,, ,,	233-35°	$C_{21}H_{16}O_6N_4$	13.0	13.3
2′,3,4′-Trihydroxy-	Orange, slender microneedles	Ethanol	224-25°	$C_{21}H_{16}O_7N_4$	12.5	12.8

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Possible Antiamoebic Agents. Part XV. Compounds Based on the Partial Structure of Aureomycin

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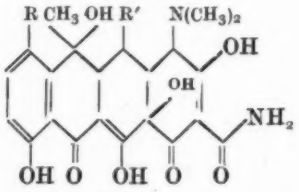
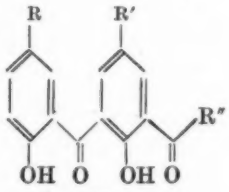
5,5′-Substituted-3-aceto-2,2′-dihydroxybenzophenones, based on the partial structure of aureomycin, have been synthesised with a view to testing their antiamoebic activity.

In recent years the antibiotics, Aureomycin (Ia) and Terramycin (Ib), are being effectively used in the treatment of amoebiasis. Their cure rate is as high as 70% (McVay *et al.*, *Science*, 1949, **109**, 590). The chemistry of these antibiotics has been elucidated by Woodward *et al.* (*J. Amer. Chem. Soc.*, 1952, **74**, 4976) and reviewed by Johnson (*Sci. Progress*, 1953, **41**, 443). These have a common ring system designated as "Tetracycline"(I).

The activity of these compounds is attributed to the presence of chelating -OH and —CO groups in the molecule (Albert *et al.*, *Med. J. Aust.*, 1944, **31**, 245; *Brit. J. Exp. Path.*, 1947, **28**, 69).



(I)



(II)

Ia: R=Cl;R′=H.
Ib: R=H;R′=OH.

In the present investigation 5,5′-substituted-3-aceto-2,2′-dihydroxybenzophenones (II) having two adjacent -CO and -OH groups, as in Aureomycin, have been synthesised with a view to studying the effect of chelation on antiamoebic activity.

The desired compounds were prepared in good yields by the Fries migration of the esters obtained from 5-substituted-2-hydroxyacetophenones with 5-substituted-2-methoxybenzoyl chlorides.

The ketonic esters as well as diketones were characterised through their 2,4-dinitrophenylhydrazones (Tables I and II).

EXPERIMENTAL

2-Methoxybenzoic acid was prepared by Dippy (*J. Chem. Soc.*, 1937, 1492) by alkaline $KMnO_4$ oxidation of the corresponding aldehyde, but the yields were not mentioned.

It has now been prepared by a modified method as follows:

2-Methoxybenzaldehyde (10 g.) (obtained by the method of Shoesmith and Connor, *J. Chem. Soc.*, 1927, 2231) was oxidised with 10% aqueous $KMnO_4$ (125 c.c.) in hot acetone (50 c.c.) solution; acetone was distilled and the remaining solution concentrated and then acidified with HCl. The precipitated acid (yield 10 g.) was recrystallised from water, m.p. 101° (Dippy, *loc. cit.*, reported m.p. 101.5°).

The above acid (6 g.) was converted to its acid chloride according to Marsh (*ibid.*, 1925, 1635), b.p. 120-25°/10mm, yield 6g.

5-Chloro-2-methoxybenzoic Acid.—Since it was found difficult to obtain the acid in a pure state by the method of Peratoner (*Gazzetta*, 1898, **28**, 211), it was prepared as follows:

5-Chloro-2-hydroxybenzaldehyde (15 g.) (prepared according to Durrans, *J. Chem. Soc.*, 1923, **123**, 1426) was methylated with methyl sulphate in 10%KOH, yielding methoxybenzaldehyde (8 g.), m.p. 82° (Buu-Hoï, *Compt. rend.*, 1945, **221**, 202, reported m.p. 81°). This aldehyde (10 g.) was oxidised with 10% aqueous $KMnO_4$ (120 c.c.) in hot acetone (50 c.c.) solution, and the resulting 5-chloro-2-methoxybenzoic acid was isolated and recrystallised from water, yield 10 g., m.p. 82-82.5° (Peratoner, *loc. cit.*, reported m.p. 81-82°).

The acid chloride of the above substance (5 g.) was prepared by the action of thionyl chloride (6 c.c.) and heating on a water bath for ½ an hour, removing the excess of the latter *in vacuo*, and recrystallising the solid acid chloride, thus obtained, from dry benzene, yield 4.5g., m.p. 62.62.5(% Cl found, 34.21; calc., 34.63).

5-Methyl-2-methoxybenzoic Acid.—Mauthner (*J. prakt. Chem.*, 1921, **103**, 295) prepared it by methylation of 5-methyl-2-hydroxybenzoic acid, but the same difficulty in obtaining the pure acid arose. It was prepared by the following method.

5-Methyl-2-methoxybenzaldehyde (10 g.) (prepared by the Gattermann reaction, as modified by Adams and Levine, *J. Amer. Chem. Soc.*, 1924, **46**, 1521) was oxidised with 5% aqueous $KMnO_4$ (220 c.c.) in acetone (50 c.c.) solution at 30-40° to yield 5-methyl-2-methoxybenzoic acid, which was crystallised from hot water, yield 9 g., m.p. 66-67° (Mauthner, *loc., cit.*, reported m.p. 66°).

This acid was converted to its acid chloride according to Mauthner (*loc. cit.*), b.p. 140-42°/10 mm, yield 80%.

2,5-Dimethoxybenzoic Acid.—Kauffmann (*Annalen*, 1905, **344**, 73) obtained it by alkaline $KMnO_4$ oxidation of 2,5 dimethoxygentisic aldehyde. The present authors obtained it by oxidising the same with aqueous $KMnO_4$ as follows:

2, 5-Dimethoxybenzaldehyde (10 g.) (prepared by the modified Gatterman reaction; cf. Gulland and Virdan, *J. Chem. Soc.*, 1928, 1481) was oxidised with 10% aqueous $KMnO_4$ (120 c.c.) in hot acetone (50c.c.) solution. Isolated as usual and recrystallised from hot water, it afforded the above acid; yield 10.2 g., m.p. 76° (Kauffmann, *loc. cit.*, reported m.p. 76°).

This acid was converted to its acid chloride in 90% yield with $SOCl_2$ as usual; b.p. 160-62°/12 mm (Mauthner, *loc. cit.*, reported b.p. 163-64°/15 mm).

5-Substituted-2-hydroxyacetophenones were obtained by first acetylating the appropriate *p*-substituted phenols with acetic anhydride (Chattaway, *J. Chem. Soc.*, 1931, 2495) and then the ester was rearranged with anhydrous $AlCl_3$ (Fries migration). The following substituted acetophenones were thus obtained:

5-Chloro-2-hydroxyacetophenone, yield 100%, m.p. 53-54° (Wittig, *Ber*, 1924, **57**, 90, reported m.p. 53.5-54.5°); 5-methyl-2-hydroxyacetophenone, yield 90% m.p. 50° (Wittig, *loc. cit.*, reported m.p. 45-46°; Rosenmund and Schnurr, *Annalen*, 1927, **460**, 83, reported m.p. 50°); 5-methyl-2-hydroxypropiophenone, yield 80%; b.p. 160°/30 mm (Auwers, *Ber.*, 1914, **47**, 7319, reported b.p. 123-24°/11 mm); 5-methoxy-2-hydroxyacetophenone, by the method of Kostanecki and Lampe (*Ber.*, 1904, **37**, 774), in 25% yield, m.p. 52°.

4,5′-Substituted-2-acetophenyl 2′-methoxybenzoates were prepared from the appropriate substituted hydroxyacetophenone (0.1*M*), anhydrous benzene (25 c.c.) and magnesium, ribbon (1 g.). The appropriate acid chloride (2 methoxy-, 2,5-dimethoxy-, 5-chloro-2-methoxy-or 5-methyl-2-methoxy-benzoyl chloride) (0.1*M*) was then added gradually and the mixture refluxed on a water bath (under $CaCl_2$ guard tube) for 4 to 5 hours. Benzene was removed under reduced pressure and the residue taken up in ether, washed with 1% NaOH, then with water, dried on anhydrous Na_2SO_4, and isolated as usual. The m.p. or b.p., yield, their 2,4 dinitrophenyl hydrazones, and their analysis are recorded in Table I.

TABLE I

No.	4,5′-Substituted-2-acetophenyl 2′-methoxybenzoate.	B.P.or M.P.	Yield.	2,4-Dinitrophenylhydrazone. M.P.	% Nitrogen. Found.	Calc.
1.	4-Methoxy	140°/14mm	65%	158°	11.84	11.66
2.	4-Methyl-2-propio	135°/14mm	65	115°	11.82	11.72
3.	4,5′Dichloro	96-97°	66	182-83°	10.66	10.46
4.	4-Methyl-5′-chloro	98°	67	142°	11.42	11.23
5.	4-Chloro-5′-methyl	78°	60	112°	11.41	11.23
6.	4,5′-Dimethyl	75°	62	130°	11.83	11.72
7.	4-Chloro-5′-methoxy	105°	65	210°	10.86	10.79
8.	4-Methyl-5′-methoxy	99°	65	225°	11.42	11.33

Migration of 4,5′-Substituted-2-acetophenyl 2-Methoxybenzoates.—The ester (1*M*) was intimately mixed in a r.b. flask with $AlCl_3$ (2 to 5*M*, anhyd.). The reaction mixture was then heated in an oil bath at 120° to 160° (Table II) for about 4 hours. The contents were decomposed with 10% ice-cold HCl, taken in ether, washed with 5% $NaHCO_3$ solution, and then with water. It was dried on anhydrous Na_2SO_4 and isolated in the usual way. The solid hydroxyketones were recrystallised from dry benzene. These were characterised through their 2,4-dinitrophenylhydrazones. During migration, demethylation of the methoxy groups also took place, thus liberating the free hydroxy group.

The physical data, yield, mols. of $AlCl_3$ used to migrate the corresponding ester, temperature of migration of ester, and analysis of the bis-2,4-dinitrophenylhydrazones of the hydroxydiketones are recorded in Table II.

TABLE II

No.	5,5′-Substituted-3-aceto-2,2′-dihydroxy-benzophenone.	B.P. or M.P.	Yield.	Mols. of $AlCl_3$ used.	Temp.	Bis-2,4-dinitrophenylhydrazone M.P.	% Nitrogen. Found.	Calc.
1.	5-Hydroxy	130°/14mm	50%	3.3	120-30°	230°	17.85	17.72
2.	5-Methyl-3-propio	140°/14mm	50	2.2	120-30°	264°	17.51	17.39
3.	5,5′-Dichloro	156-57°	65	3.3	120-30°	262°	16.48	16.35
4.	5-Methyl-5′-chloro	169°	63	3.3	120-30°	252°	16.98	16.85
5.	5-Chloro-5′-methyl	148°	55	3.3	120-30°	211°	16.97	17.55
6.	5,5′-Dimethyl	146°	56	3.3	120-30°	205°	17.51	17.55
7.	5-Chloro-5′-hydroxy	171°	62	5.5	130-40°4hr. 140-60°1hr.	267°	16.90	16.80
8.	5-Methyl-5′-hydroxy	182°	65	5.5	,,	250°	17.48	17.33

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The Chemistry of Natural Products. Part I. Chemical Studies on Erythrophlamic Acid

Vishwa Prakash Arya

Degradative experiments support structure (I) for erythrophlamic acid.

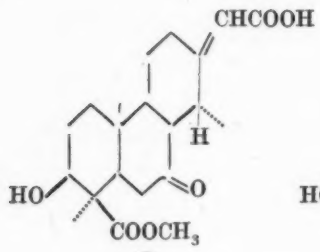
Erythrophlamic acid is a diterpene acid related to other diterpenoids isolated from the bark of *Erythrophleum guineense* G. Don. It occurs as an ester of *N*,*N*-dimethylaminoethanol, the resulting base being known as erythrophlamine (Engel *et al.*, *Rec. trav. chim.*, 1950, **69**, 396). Erythrophlamic acid contains one double bond $\alpha\beta$ to the carboxyl group, one keto group, one hydroxyl group, and a sterically hindered methoxycarbonyl group (Mathieson *et al.*, *Exper.*, 1960, **16**, 404). The structure of this acid has been shown to be (I) on the basis of its conversion to 3β, 7β-dihydroxycassanic acid (II) (Arya and Engel, *Helv. Chim. Acta*, in press). This communication deals with some chemical studies on erythrophlamic acid carried out prior to the complete elucidation of its structure (Arya, Ph. D. Thesis, London University, 1959, pp. 171-181).

Erythrophlamic acid exhibited infrared bands at 3540, 1710, 1680, and 1640 cm^{-1}. These bands are characteristic, respectively, of a hydroxyl group, a methoxycarbonyl group superimposed on a six-membered ring carbonyl, a carboxyl group of an $\alpha\beta$-unsaturated acid, and the double bond of this group. Treatment of erythrophlamic acid in methanol with ethereal diazomethane gave methyl erythrophlamate. The infrared spectrum of this compound in bromoform solution showed bands at 3520 cm^{-1} (hydroxyl, 3580 cm^{-1} in CCl_4), 1705 cm^{-1} (methoxycarbonyl groups superimposed on a six-membered ring carbonyl, 1710 cm^{-1} in CCl_4), and at 1650 cm^{-1} (double bond of an $\alpha\beta$-unsaturated ester). Methyl erythrophlamate formed a mono-acetate. The infrared spectrum of methyl erythrophlamate in carbon tetrachloride solution had bands at 1740, 1240 cm^{-1} (acetate), 1725 cm^{-1} (carbomethoxyl groups superimposed on a six-membered ring carbonyl), and at 1650 cm^{-1} (double bond of an $\alpha\beta$-unsaturated ester).

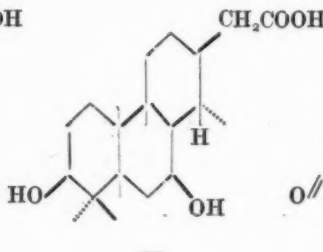
When methyl erythrophlamate was oxidised with chromic anhydride in acetic acid, it formed methyl dehydroerythrophlamate (III), $C_{22}H_{30}O_6$. The ultraviolet absorption spectrum of this compound was typical of an $\alpha\beta$-unsaturated ester (λ_{max} 221 mμ; log ϵ 4.27). The infrared spectrum supported this view and showed bands in chloroform solution at 1710 and 1650 cm^{-1}. Methyl dehydroerythrophlamate gave a positive Zimmermann test indicating the presence of a 3-oxo grouping (Barton and Mayo, *J. Chem. Soc.*, 1954, 887).

Sodium borohydride reduced erythrophlamic acid to a dihydroxy acid (IV), $C_{21}H_{32}O_6$, in which the conjugated double bond was still present (λ_{max} 219 mμ; log ϵ 4.21). A Zerewitinoff estimation in a mixture of *N*-methyl-1,2,3,4-tetrahydroquinoline and di-

isoamyl ether as solvent indicated the presence of three active hydrogens (for method of estimation, see Perold and Snyman, *Mikrochim. Acta*, 1958, 225).



(I)



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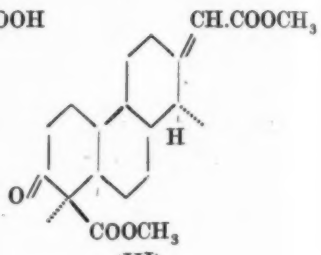

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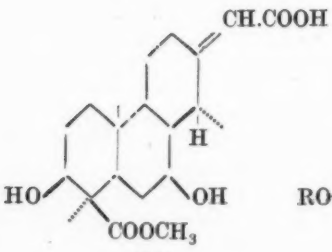

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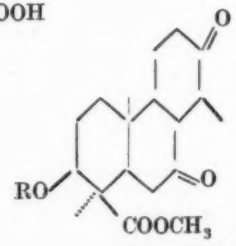
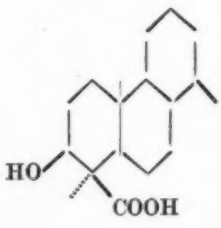


(V) a. R=H
b. R=Ac



(VI)

Ozonolysis of erythrophlamic acid or methyl erythrophlamate at -50° to -70° in chloroform solution afforded a hydroxydiketone (Va: R=H), $C_{19}H_{28}O_5$. The infrared absorption spectrum of this compound showed strong bands at 3500 cm^{-1} (hydroxyl) and 1712 cm^{-1} (methoxycarbonyl group superimposed on two cyclohexanone type carbonyls). Similarly ozonolysis of methyl erythrophlamate acetate yielded an acetoxydiketone (Vb: R=Ac), $C_{21}H_{30}O_6$. Oxalic acid was also obtained in about 20% yield. The isolation of the latter confirms the nature of the side-chain which is the same as in cassaic acid (Arya and Mathieson, *J. Chem. Soc.*, 1959, 3623). The diketone (Vb) formed a bis-2, 4-dinitrophenylhydrazone. Mild alkaline hydrolysis of (Vb) furnished the hydroxydiketone (Va) (mixed m.p. showing no depression).

The Wolff-Kishner reduction of the hydroxydiketone (Va) under strictly anhydrous conditions (Barton *et al.*, *J. Chem. Soc.*, 1955, 2056) afforded a crystalline hydroxy-acid (VI) in a small quantity. Concomitant hydrolysis of the sterically hindered methoxycarbonyl group took place. These results together with spectral evidence support the structure (I) for erythrophlamic acid.

EXPERIMENTAL

Melting points are uncorrected. Optical rotations and ultraviolet absorption spectra were determined in 95% ethanol, unless otherwise stated. Light petroleum refers to the fraction of petroleum having the boiling range of 40-60°.

Erythrophlamic Acid (I).—Methyl erythrophlamate (40 mg.) in 2*N* ethanolic KOH solution (5 c.c.) was refluxed on a steam bath for 2 hrs. The solution was cooled to 0° and acidified with 2*N*-HCl (7.5 c.c.), when crystals appeared. These were collected, dried, and weighed. It (35 mg.) was recrystallised from methanol-water, m.p. 218-20°, $[\alpha]^{20}_{D}$-62° (*c*=1) (Lit. cites m. p. 218-20°). UV spectrum: λ_{max} 223 mμ; log ε 4.20. IR spectrum (in nujol mull): strong bands at 3540, 1710, 1680, 1640 cm^{-1}. (Found: C, 66.43; H, 7.77; O,25.73; OMe, 8.67. Calc. for $C_{21}H_{30}O_6$: C, 66.64; H 7.99; O,25.37; OMe, 8.20%).

Methyl Erythrophlamate.—Erythrophlamic acid (10 mg.) in methanol (2 c.c.) was treated with an excess of ethereal diazomethane. On working up in the usual manner, a crystalline residue (9.9 mg.) was obtained which crystallised from methanol-ether, m.p. 175-76°, $[\alpha]_D^{21} = -67°$ (*c*=0.5) (Lit. cites m.p. 177°). (Found: C, 67.42.; H, 7.99; OMe, 16.11. Calc. for $C_{22}H_{32}O_6$: C, 67.32;H, 8.22; OMe 15.86%).

UV spectrum: λ_{max} 223 mμ; log ε 4.30. IR spectrum (in $CHBr_3$ solution): strong bands at 3540, 1705, 1650 cm^{-1}. (in CCl_4 solution), strong bands at 3580, 1710, 1650 cm^{-1}.

Treatment of the ester in *N*-methyl-1,2,3,4-tetrahydroquinoline with excess of methylmagnesium iodide in di-isoamyl ether gave methane equivalent to 0.94 active hydrogen.

Methyl Erythrophlamate Acetate.—Methyl erythrophlamate (80 mg.) in anhydrous pyridine (5 c.c.) and acetic anhydride (1 c.c.) were warmed on a steam bath for 1 hr. and left at room temperature overnight. When the reaction mixture was worked up in the usual manner, a gummy acetate (86 mg.) resulted. It was twice sublimed in high vacuum (2×10^{-5} mm) at 170°. The sublimate crystallised from ether, m. p. 171°, $[\alpha]^{22}_{D}$ -59 (*c*=1, $CHCl_3$) (Lit. cites m.p. 173°). (Found: C, 65.18; H 7.90; COMe, 10.5. Calc for $C_{21}H_{34}O_7$: C, 65.38; H, 8.11; -$COCH_3$, 9.9%).

UV spectrum: λ_{max} 223 mμ; log ε 4.21. IR spectrum (in CCl_4 solution): strong bands at 1740, 1725, 1650, and 1240 cm^{-1}. No methane was evolved on treatment with methylmagnesium iodide in di-isoamyl ether.

Methyl Dehydroerythrophlamate (III).—Methyl erythrophlamate (80 mg.) in glacial acetic acid (10 c.c.) was added to a suspension of chromic anhydride (20 mg.) in acetic acid (5 c.c.) at 45°. The reaction was allowed to proceed at room temperature overnight. It was then poured into water and extracted with ether; on working up in the usual manner it gave a crystalline residue (77 mg.) This was crystallised first from petroleum (60-80°) and then twice from ether-light petroleum, m.p. 133-34°, $[\alpha]_D$ -101° (*c*=1). (Found: C, 67.57; H, 7.93; O, 24.58; OMe, 15.81. $C_{22}H_{30}O_6$ requires. C, 67.66; H, 7.75; O, 24.59; OMe, 15.90%).

UV spectrum: λ_{max} 221 mμ; log ε 4.27. IR spectrum (in $CHCl_3$ solution): strong bands at 1710, 1650 cm^{-1}. This compound gave positive tetranitromethane, Zimmermann, and Liebermann-Burchard tests. Methane was not evolved on treatment with methylmagnesium iodide in di-isoamyl ether.

Sodium Borohydride Reduction of Erythrophlamic Acid.—Erythrophlamic acid (10.2 mg.) in absolute methanol (3 c.c.) was treated with sodium borohydride (5.1 mg.) in water

(0.8 c.c.). On working up in the usual manner it gave a crystalline residue, m.p. 235-38°, which was recrystallised from methanol to furnish the pure *dihydroxy acid* (IV), m.p. 273-74°. UV spectrum: λ_{max} 219 mμ; log ε 4.21. (Found: C, 66.21; H, 8.32. $C_{21}H_{32}O_6$ requires C, 66.21; H 8.48%).

Treatment of the dihydroxy-acid in *N*-methyl-1,2,3,4-tetrahydroquinoline with excess of methylmagnesium iodide in di-isoamyl ether gave methane equivalent to 3 active hydrogens.

Ozonolysis of Methyl Erythrophlamate.—Methyl erythrophlamate (37 mg.) in dry chloroform (20 c.c.) was ozonised with an oxygen-ozone mixture (19:1) for 30 mins. at -50° to -70°. The bluish ozonide solution was allowed to warm to room temperature, then evaporated to dryness at the steam bath under reduced pressure.

The gummy ozonide was shaken with zinc powder (500 mg.), glacial acetic acid (10 c.c.) and water (5 c.c.) for 2 hrs. Unchanged metal was filtered and the filtrate worked up in the usual manner to give a crystalline residue (21 mg.). Three recrystallisations from ether—light petroleum gave colorless needles of the *hydroxydiketone* (Va), m.p. 211-12°. (Found: C, 67.95; H, 8.10. $C_{19}H_{28}O_5$ requires C, 67.82; H, 8.38%). IR spectrum (in $CHCl_3$ solution): 3500, 1712 cm^{-1}.

This compound gave a positive Zimmermann test. When erythrophlamic acid (20 mg.) was ozonised under identical conditions, it furnished the same hydroxydiketone (Va) (12 mg.) (superimposable IR spectra).

Ozonolysis of Methyl Erythrophlamate Acetate.—Methyl erythrophlamate acetate (30 mg.) in chloroform (30 c.c.) was ozonised for 30 mins. at -50° to -70°. The bluish ozonide solution was worked up in the manner described above to furnish a gummy residue (21 mg.). This was crystallised three times from ether—light petroleum to furnish the needles of the *acetoxydiketone* (Vb), m.p. 182-83°. IR spectrum (in $CHCl_3$ solution): Strong bands at 1740, 1715, 1240 cm^{-1}. (Found: C, 66.97; H, 7.79; O, 24.87. $C_{21}H_{30}O_6$ requirers C, 66.64; H, 7.99; and 0, 25.37%).

The acetoxydiketone (Vb) formed a *bis-2,4-dinitrophenylhydrazone* in orange needles from ethyl acetate—ethanol, m.p. 271° (decomp.). UV spectrum: λ_{max} 360 mμ; log ε 4.59 ($CHCl_3$). (Found: N, 14.37. $C_{33}H_{38}O_{12}N_8$ requires N,14.83%).

Isolation of Oxalic Acid from the Ozonolysis Products of Methyl Erythrophlamate Acetate.—The acidic fraction from the above ozonolysis was saponified with 2*N*-NaOH, cooled to room temperature, and acidified with 2*N*-HCl. The acidified solution was extracted with ether in a liquid/liquid extractor for 3 days. On working up the resulting ethereal extract, a brown gum (16 mg.) was obtained. This was sublimed three times at 180°/0.1 mm and the sublimate (6 mg.) had m.p. 187-89°; mixed m.p. with an authentic sample of oxalic acid, 187-89°.

Hydrolysis of the Acetoxydiketone (Vb).—The acetoxydiketone (Vb) (5mg.) in absolute ethanol (5 c.c.) and 2*N*-KOH (3 drops) was boiled under reflux for 2 hrs. and worked up in the usual manner to give a gum (3 mg.). This product, after two crystallisations gave colorless needles, m.p. 210.5-12°. The mixed m.p. with the hydroxydiketone (Va) was undepressed.

Wolff-Kishner Reduction of Hydroxydiketone (Va).—The hydroxydiketone(Va) (40 mg.) was refluxed for 48 hours at 210° with redistilled diethylene glycol (10 c.c.), sodium (20 mg.), and an excess of anhydrous hydrazine. The reaction mixture was cooled to room temperature and worked up in the usual way. A brown gummy residue (28 mg.) resulted, which was treated with charcoal in methanol and filtered through a column of silica gel (2 g.) using chloroform as the solvent. It was obtained as a colorless gum which crystallised very slowly to give fine needles of the *hydroxy-acid* (VI), m.p. 231-32°. IR spectrum (in $CHCl_3$ solution): 3500, 1670 cm^{-1}. (Found: C, 73.10; H,10.19. $C_{18}H_{30}O_3$ requires C, 73.43; H, 10.27%).

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Action of Yeast Invertase on Different Substrates

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A sample of invertase has been prepared from brewer's yeast which hydrolyses inulin, sucrose, and raffinose to a considerable degree. Behaviour of this invertase has been found towards inulin to be of a specific character.

The work of Adams *et al.* (*J. Amer. Chem. Soc.*, 1943, **65**, 1369) has proved the presence of some specific enzymes in certain highly purified invertase preparations. These authors studied the behaviour of several yeast invertase preparations towards substrates containing both sucrose and glycosidic linkages. In their experiments enzymatic hydrolysis with five highly purified invertase preparations were tried on twentyeight carbohydrate substrates and at least four distinct types of invertase were detected, which differed in their behaviour towards the substrates, e.g., sucrose, raffinose, stachyose, inulin, melibiose, and β-phenyl-D-mannoside. These authors observed that the fructofuranoside linkages in the carbohydrate substrates, sucrose and raffinose, were hydrolysed by the same type of invertase preparation and that the common enzyme β-D-fructofuranosidase was responsible for this hydrolysis. There is evidence also of the presence of another enzyme, inulase, which is responsible for the hydrolysis of inulin. This is against what may be expected of the original postulation of Weidenhagen who assumed the hydrolysis to be done by the same β-D-fructofuranosidase. Different rates and ratios of hydrolysis by the various invertase preparations and different optimum *p*H values suggested the presence of more than one distinct enzyme in the invertase preparations. The methods of purification of invertase involved the use of bentonite in most cases. The author demonstrated the superior adsorption capacity of invertase, purified from ethanol in the cold, as compared with bentonite-purified samples. This ethanol-purified sample has been used in the present investigation to study the relative hydrolytic behaviour of the three carbohydrates and results so obtained have been compared with those by Adams *et al.* and others. The object of such a comparison is to find out the special features of the relative hydrolytic behaviour of the substrates due to the same enzyme preparation, which is precipitated by ethanol in a sufficiently pure condition. Such a study is expected to furnish a clue to the chemical nature of this enzyme preparation.

EXPERIMENTAL

Dried brewer's yeast powder (1320 g.) was treated with toluol (132 c.c.) and distilled water (1980 c.c.); the mixture was kept at 35° for 4 days. After this period of autolysis the mixture was diluted with distilled water (1800 c.c.) and filtered with kieselguhr under suction. The clear filtrate was put to a dialyser at 35°, fed with running tap water, and dialysis carried on for 48 hours using toluol to prevent putrefaction. The dialysed invertase extract (890 c.c.) was treated with an equal volume of absolute ethanol at *p*H 4.5, kept in

the cold (0-5°), and centrifuged. The precipitate was thereafter dissolved in 460 c.c. of water. Percentage of protein in this solution was 2.97. The original yeast powder (10 g.) was found to be equivalent to 11.4 c.c. of this invertase solution. The invertase activity was measured by the amount of reducing sugar formed by the enzyme which was determined by titration with Benedict's reagent. Titres corresponding to 10 g. yeast were calculated. The results are recorded in Tables I—III and in Fig 1.

The optimum percentage of inulin was found to be 20 g. in 200 c.c. of water to yield a comparable figure for the amount of reducing sugar liberated by the enzyme.

TABLE I

Substrate=sucrose (80 g.). Temp.=37.4°. Water=200 c.c. NaH_2PO_4 soln.=25 c.c. Toluol=2 c.c.

Enzyme solution (2.97%).	Distilled water.	Invertase activity for 10 g. yeast powder (g.sugar)	Enzyme solution (2.97%).	Distilled water.	Invertase activity for 10g. yeast powder (g. sugar).
0.0 c.c.	20.0 c.c.	..	12.0 c.c.	8.0 c.c.	1.36 g.
2.0	18.0	5.17 g.	14.0	6.0	1.24
4.0	16.0	2.79	16.0	4.0	1.16
6.0	14.0	2.11	18.0	2.0	1.10
8.0	12.0	1.66	20.0	0.0	1.07
10.0	10.0	1.55			

N. B. *p*H remained at 4.8 sharp both before and after treatment.

TABLE II

Substrate=inulin (20 g.). Other conditions same as in Table I.

Enzyme soln. (2.97%)	Distilled water.	Invertase activity for 10 g. yeast powder (g.sugar).	Enzyme soln. (2.97%).	Distilled water.	Invertase activity for 10 g. yeast powder (g. sugar).
0.0 c.c.	20.0 c.c.	..	12.0. c.c.	8.0 c.c.	3.75 g.
2.0	18.0	17.90 g.	14.0	6.0	3.43
4.0	16.0	9.18	16.0	4.0	3.35
6.0	14.0	6.46	18.0	2.0	3.10
8.0	12.0	5.13	20.0	0.0	3.17
10.0	10.0	4.23			

N. B. *p*H remained at 5.0 exactly both before and after treatment.

TABLE III

Substrate=raffinose (20g.). Other conditions same as in Table I.

Enzyme soln. (2.97%).	Distilled water.	Invertase activity for 10 g. yeast (g. sugar)	Enzyme soln. (2.97%).	Distilled water.	Invertase activity for 10g. yeast (g. sugar).
0.0 c.c.	20.0 c.c.	..	12.0 c.c.	8.0 c.c.	1.16 g.
2.0	18.0	3.10 g.	14.0	6.0	1.24
4.0	16.0	1.74	16.0	4.0	1.21
6.0	14.0	1.36	18.0	2.0	1.25
8.0	12.0	1.24	20.0	0.0	1.29
10.0	10.0	1.16			

N. B. *p*H remained at 4.6 exactly both before and after treatment.

DISCUSSION

Fig. 1 (vide Tables I-III) represents the behaviour of purified invertase solution towards sucrose, raffinose, and inulin as substrates. The abscissae represent volumes of enzyme solution (2.97%) per 20 c.c. and the ordinates represent the enzyme activities for the substrates as measured by the amounts of reducing sugar liberated by the enzyme extract corresponding to 10 g. of brewer's yeast. Varying proportions of enzyme solution were used and activities corresponding to 10g. yeast powder calculated in each case. If there was no influence of the concentration of the enzyme on the substrate the activity curves should have been straight lines. But the graphs as drawn in the figure appear to be otherwise.

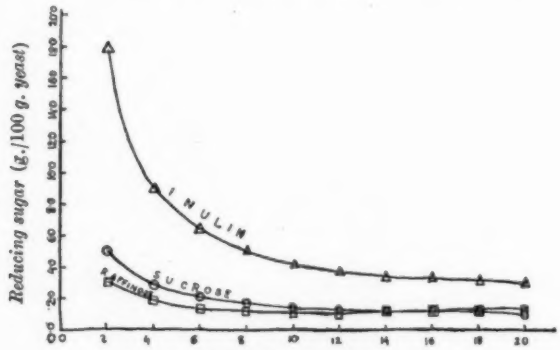

FIG. 1

The curve for inulin is much steeper than those for sucrose and raffinose. The curves for sucrose and raffinose are practically similar, the former being slightly steeper. The steepness of the curve for inulin suggests a higher rate of hydrolysis of the substrate at the initial concentrations of enzyme. Although inulin possesses considerable reducing power on Benedict's solution initially, the curves for sucrose and raffinose indicate a lower activity towards the enzyme. Thus there is some reasons to anticipate a decidedly distinct bahaviour on the part of sucrose and raffinose as substrates, as compared with inulin. The work of Adams *et al.* (*loc. cit.*) has suggested the presence of a specific enzyme, inulase, in some of the enzyme preparations which behaves towards inulin in a specific way. Sreenivasya and Iyengar (*Nature*, 1933, **132,** 604) effected a partial separation of invertase and inulase. The curve of inulin (Fig. 1) also suggests a specific behaviour of the invertase preparation from brewers' yeast towards inulin as compared with sucrose and raffinose, which practically belong to the same category.

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Amino Derivatives of Tellurium Tetrachloride. Part I

Sarju Prasad and Bishan Lal Khandelwal

The amino derivatives of tellurium tetrachloride have been prepared by the action of tellurium tetrachloride on some mono- and diamines in benzene medium. Properties of the derivatives have been studied and structures discussed.

Lowy and Dunbrook (*J. Amer. Chem. Soc.*, 1922, **44**, 614) prepared $(C_6H_5NH_2)_2.TeBr_4$, $(BrC_6H_4NH_2)_2.TeBr_4$, $(C_{10}H_7NH_2)_2.TeBr_4$, $C_6H_4(NH_2)_2.TeBr_4$, $C_7H_6(NH_2)_2.TeBr_4$, $NH_2C_6H_4C_6H_4NH_2.TeBr_4$ compounds of tellurium tetrachloride with aniline, *p*-bromoaniline, β naphthylamine, *p*-phenylenediamine, *m*-tolylenediamine, and benzidine respectively in glacial acetic acid or in dry ether medium. By passing anhydrous ammonia gas on $TeCl_4$, Strecker and Ebert (*Ber.*, 1925, **58**, 2527) obtained $TeCl_4.6NH_3$ at 0°as a white, hygroscopic compound. Recently, Tronev and Grigorovich (*Zhur. Neorg. Khim.*, 1957, **2**, 2400) prepared $TeCl_4.4NH_3$ and $TeCl_4.6NH_3$ by the action of anhydrous ammonia gas at 6 to 8 atmosphere pressure on anhydrous $TeCl_4$ and $TeCl_4.2en$, $TeCl_4.2en.2NH_3$, $TeCl_4.2PhNH_2$, $TeCl_4.2PhNH_2.2NH_3$, and $TeCl_4.2py$ by mixing amine and $TeCl_4$ solutions in C_6H_6, MeOH, or acetone.

The present investigation has been undertaken with a view to studying the formation of compounds of tellurium tetrachloride with aromatic primary amines in benzene.

EXPERIMENTAL

Tellurium tetrachloride was prepared from its elements and purified by distillation. The other chemicals used were of E. Merck or B. D. H. 'extra pure' quality.

General Method of Preparation.—A solution of the amine in benzene was slowly added to a solution of tellurium tetrachloride in benzene with constant shaking till complete precipitation. The amine solution was then added in slight excess and the mixture left for about an hour. The precipitate was filtered and washed with benzene till the washings ceased to form any precipitate with tellurium tetrachloride solution. It was dried at the room temperature in a vacuum desiccator, analysed, and its properties were studied.

Tellurium was estimated as TeO_2, chlorine by Piria and Schiff's method after removing tellurium, and nitrogen by Dumas' method.

The compounds of tellurium tetrachloride prepared with mono- and diamines are listed in Tables I and II.

General Properties.—The compounds are coloured, amorphous, insoluble in carbon tetrachloride, ether, ethanol, acetone, etc. but readily soluble in dilute acids. The compounds obtained with *m*-toluidine, *o*-toluidine, and *o*-phenylenediamine are sparingly soluble in

TABLE I

Compounds of tellurium tetrachloride with primary monoamines.

Amine.	Compound formed.	Colour.	M.P*	%Tellurium.		%Chlorine.		%Nitrogen.	
				Found.	Calc.	Found.	Calc.	Found.	Calc.
Benzylamine	$(C_6H_5CH_2NH_2)_2.TeCl_4$	Dirty yellow	105°	25.93	26.39	29.31	29.36	5.72	5.79
o-Toluidine	$(CH_3C_6H_4NH_2)_2.TeCl_4$	Lemon yellow	125°	26.27	26.39	29.28	29.36	5.73	5.79
m-Toluidine	$(CH_3C_6H_4NH_2)_2.TeCl_4$	Greenish violet	144°	26.26	26.39	29.29	29.36	5.72	5.79
o-Anisidine	$(CH_3OC_6H_4NH_2)_2.TeCl_4$	Grey	128°	24.84	24.75	27.31	27.54	5.45	5.43
m-Anisidine	$(CH_3OC_6H_4NH_2)_2.TeCl_4$	Yellow	115°	24.63	24.75	27.48	27.54	5.22	5.43
o-Phenetidine	$(C_2H_5OC_6H_4NH_2)_2.TeCl_4$	Dirty yellow	102°	23.26	23.47	25.91	26.12	4.97	5.15
p-Phenetidine	$(C_2H_5OC_6H_4NH_2)_2.TeCl_4$	Pinkish white	132°	23.12	23.47	26.00	26.12	4.98	5.15
p-Toluidine	$(CH_3C_6H_4NH_2)_2.TeCl_4$	Yellow	142°	26.28	26.39	29.28	29.36	5.69	5.79
p-Anisidine	$(CH_3OC_6H_4NH_2)_2.TeCl_4$	Red	137°	24.81	24.75	27.45	27.54	5.36	5.43
β-Naphthylamine	$(C_{10}H_7NH_2)_2.TeCl_4$	Brownish black	138°	23.08	22.97	25.61	25.56	4.93	5.04

TABLE II

Compounds of tellurium tetrachloride with primary diamines.

Amine.	Compound formed.	Colour.	M.P.*	%Tellurium.		%Chlorine.		%Nitrogen.	
				Found.	Calc.	Found.	Calc.	Found.	Calc.
Benzidine	$(NH_2C_6H_4C_6H_4NH_2).TeCl_4$	Greyish white	212°	27.91	28.13	31.12	31.30	6.14	6.17
o-Phenylenediamine	$[C_6H_4(NH_2)_2].TeCl_4$	Pink	168°	33.68	33.79	37.48	37.60	7.33	7.41
m-Phenylenediamine	$[C_6H_4(NH_2)_2].TeCl_4$	Yellow	165°	33.65	33.79	37.52	37.60	7.31	7.41
o-Tolidine	$(CH_3NH_2C_6H_3C_6H_3NH_2CH_3)$-$TeCl_4$	Yellowish white	187°	26.57	26.49	29.35	29.48	5.76	5.81
Dianisidine	$(CH_3O(NH_2)C_6H_3C_6H_3(NH_2)$-$OCH_3).TeCl_4$	Do	158°	24.81	24.84	27.59	27.67	5.23	5.45

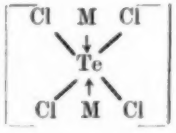
*Melt with the decomposition.

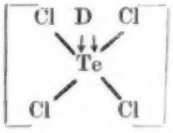
acetone. These compounds are fairly stable in dry air, but decompose slowly in presence of moisture with the formation of tellurous acid. All these compounds add up ammonia molecules when suspended in benzene and dry gas is passed through them.

On heating alone they furnish white or greyish white sublimate, which is soluble in water, acidic, and responds to the tests for chlorine and amino group. Derivatives of monoamines afford the sublimate at lower temperatures than those with the diamines. When heated with soda-lime, the corresponding amines separate and condense in the cooler parts of the tube. All these compounds respond to the diazo test.

DISCUSSION

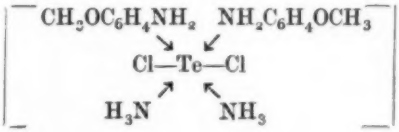
As evident from the results, the number of molecules of the amine, which combine with one mol. of $TeCl_4$, depends on the number of amino groups in the molecule. In all the cases studied, two molecules of a monoamine are or one molecule of a diamine is attached to one molecule of $TeCl_4$. The compounds may be represented as



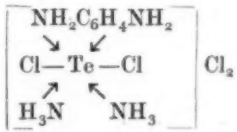


in case of mono- or diamines respectively (where M = monoamine and D = diamine).

Further, addition of two molecules of NH_3, as found on analysing the compounds formed with bis-*o*-anisidine tetetrachloride (Found: Te, 23.08; Cl, 25.67; N, 9.88. $TeCl_4 \cdot 2CH_3OC_6H_4NH_2 \cdot 2NH_3$ requires Te, 23.22; Cl, 25.83; N, 10.19%) and with *o*-phenylenediamine tetetrachloride [Found: Te, 30.91; Cl, 34.27; N, 13.42. $TeCl_4 \cdot C_6H_4(NH_2)_2 \cdot 2NH_3$ requires Te, 31.00; Cl, 34.49; N, 13.60%] displaces two atoms of chlorine, keeping the maximum covalency of tellurium as 6, whereas the amine molecules fail to do so due to steric hindrance. These compounds may be represented as



and



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Melt with the decomposition.

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Chemistry of Thorium. Part I. Amino Derivatives of Thorium (IV) Chloride

Sarju Prasad and Suresh Kumar

The amino derivatives of thorium (IV) chloride have been prepared by the action of $ThCl_4$ on some aromatic primary (mono- and di-) amines; their properties have been studied and structures discussed.

Matthews (*J. Amer. Chem. Soc.*, 1898, **24**, 815) obtained a number of amino derivatives of thorium chloride by the action of $ThCl_4$ on ammonia and respective bases in ether and also those of $ThBr_4$ by the action of solid $ThBr_4$ on gaseous ammonia and the respective amine.

Chauvenet (*Compt. rend.*, 1911, **151**, 387) studied the action of $ThCl_4$ on liquid and gaseous ammonia and reported the formation of a number of ammines which gave $Th(NH_2)_4$ at 250-300° and $Th(NH)_2$ at red heat.

Brintzinger and Hesse (*Z. anorg. Chem.*, 1944, **252**, 293) reported formation of a number of co-ordination compounds of $ThCl_4$ on some aliphatic amines.

Fowles and Pollard (*J. Chem. Soc.*, 1953, 4128) obtained the hexammine, $ThCl_4.6NH_3$, by the action of NH_3 on $ThCl_4$ at -36°.

No systemic work appears to have been done on the reactions of $ThCl_4$ with aromatic amines. The present investigation was therefore undertaken with a view to studying the formation of compounds of thorium tetrachloride with aromatic primary mono- and diamines in anhydrous ether.

EXPERIMENTAL

Anhydrous thorium (IV) chloride was prepared by the method of Dean and Chandler (*Nuclear Sci. & Eng.*, 1957, **2**, 57), extracted with anhydrous ether (distilled over sodium metal), and analysed for purity. The amines and other chemicals used were of B. D. H. (A. R.) or E. Merck's E. P. quality.

In all the cases moderately dilute ethereal solution of amine was slowly added to the ethereal solution of $ThCl_4$ with constant shaking till complete precipitation. It was allowed to stand for an hour in a desiccator, filtered, and washed with ether till free of the reactants. The precipitate was dried over fused calcium chloride in a vacuum desiccator at the room temperature and analysed.

Thorium was estimated as ThO_2 by charring a weighed quantity of the compound with H_2SO_4 (conc.) followed by oxidation of the organic matter with HNO_3 (conc.) and subsequently precipitating $Th(OH)_4$ by an excess of NH_4OH. The precipitate was filtered, washed

TABLE I

Compounds of thorium (IV) *chloride with aromatic primary monoamines.*

No.	Amines.		Temp.	%Thorium. Found.	%Thorium. Calc.	%Chlorine. Found.	%Chlorine. Calc.	%Nitrogen. Found.	%Nitrogen. Calc.	Probable formula.
1.	Benzylamine	M.p.	240°	28.48	28.94	17.56	17.70	6.87	6.98	$[Th(C_6H_5CH_2NH_2)_4]Cl_4$
2.	*o*-Toluidine	,,	175°	28.56	28.94	17.76	17.70	6.73	6.98	$[Th(C_6H_4CH_3NH_2)_4]Cl_4$
3.	*p*-Toluidine	Decomp.	198°	28.63	28.94	17.53	17.70	6.89	6.98	$[Th(C_6H_4CH_3NH_2)_4]Cl_4$
4.	*m*-Toluidine	,,	185°	28.73	28.94	17.46	17.70	6.74	6.98	$[Th(C_6H_4CH_3NH_2)_4]Cl_4$
5.	*o*-Anisidine	,,	175°	26.89	26.79	16.13	16.39	6.23	6.46	$[Th(CH_3OC_6H_4NH_2)_4]Cl_4$
6.	*p*-Anisidine	,,	193°	26.52	26.79	16.27	16.39	6.29	6.46	$[Th(CH_3OC_6H_4NH_2)_4]Cl_4$
7.	*m*-Anisidine	,,	134°	26.47	26.79	16.03	16.39	6.18	6.46	$[Th(CH_3OC_6H_4NH_2)_4]Cl_4$
8.	*o*-Phenetidine	,,	143°	24.78	25.17	14.99	15.39	5.84	6.07	$[Th(C_2H_5OC_6H_4NH_2)_4]Cl_4$
9.	*p*-Phenetidine	,,	204°	24.95	25.17	14.88	15.39	5.76	6.07	$[Th(C_2H_5OC_6H_4NH_2)_4]Cl_4$
10.	α-Naphthylamine	,,	222°	24.09	24.53	14.64	15.08	5.58	5.92	$[Th(C_{10}H_7NH_2)_4]Cl_4$
11.	β-Napththylamine	,,	170°	24.67	24.53	14.76	15.08	5.64	5.92	$[Th(C_{10}H_7NH_2)_4]Cl_4$

TABLE II

Compounds of thorium (IV) *chloride with aromatic primary diamines.*

No.	Diamines.		Temp.	%Thorium. Found.	%Thorium. Calc.	%Chlorine. Found.	%Chlorine. Calc.	%Nitrogen. Found.	%Nitrogen. Calc.	Probable formula.
1.	*o*-Phenylenediamine	Decomp.	165°	39.59	39.33	23.74	24.06	9.21	9.48	$[Th(H_2NC_6H_4NH_2)_2]Cl_4$
2.	*p*-Phenylenediamine	,,	240°	38.87	39.33	23.65	24.06	9.12	9.48	$[Th(H_2NC_6H_4NH_2)_2]_4Cl_4$
3.	*m*-Phenylenediamine	,,	170°	38.91	39.33	24.37	24.06	9.07	9.48	$[Th(H_2NC_6H_4NH_2)_2]Cl_4$
4.	Phenylhydrazine	,,	190°	28.38	28.79	17.08	17.61	6.53	6.94	$[Th(C_6H_5NHNH_2)_4]Cl_4$
5.	Benzidine	,,	240°	31.56	31.27	18.80	19.13	7.19	7.54	$[Th(H_2NC_6H_4\text{-}C_6H_4NH_2)_2]Cl_4$
6.	*o*-Dianisidine	,,	235°	26.43	26.92	16.23	16.47	6.03	6.49	$[Th(CH_3O.NH_2.C_6H_3C_6H_3\text{-}NH_2.OCH_3)_2]Cl_4$
7.	*o*-Tolidine	,,	250°	28.56	29.08	17.36	17.79	6.71	7.02	$[Th(CH_3.NH_2.C_6H_3C_6H_3NH_2CH_3)_2]Cl_4$

thoroughly, dried, ignited to ThO_2, and weighed. Chlorine was estimated by Piria and Schiff's method as AgCl and nitrogen by Kjeldahl's method.

General Properties.—All the compounds are coloured, amorphous, insoluble in ether, CCl_4, $CHCl_3$, and benzene but sparingly soluble in acetone. These are stable in dry atmosphere but decompose on long exposure to moist air and are hydrolysed when boiled with water or strong alkali solution; but cold water is without action [these dissolve slowly in HNO_3 (dil.) and immediately in HNO_3 (conc)]. On heating these decompose, generally with melting, but in a few cases decompose without melting. Benzylamine and *o*-toluidine compounds have sharp melting points. On heating with soda-lime the corresponding amines are liberated and condensed in the cooler parts of the tube. On heating alone these furnish white, grey, brown, or yellow sublimates which respond to the tests for $-NH_2$ and Cl groups. These compounds respond to the diazo test. Compounds with diamines are more stable than those with monoamines.

DISCUSSION

The co-ordination number of thorium in these compounds is four and chelate compounds are formed in case of diamines, which are perhaps responsible for their greater stability. Though maximum co-ordination number (8) for thorium is not attained, compounds are very stable, probably due to symmetrical structure. These compounds may be represented as $[Th.4M]Cl_4$ and $[Th.2D]Cl_4$, where M=a monoamine and D=a diamine molecule.

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Photolytic Separation of Uranium from Thorium, Zirconium, and Manganese

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Separation of uranium from thorium, zirconium, and manganese has been effected by photochemical process using their sulphate solution. Role of alcohol on the recovery of uranium has been investigated.

The photolytic separation of uranium from vanadium using sulphate solutions, reported earlier (Mishra *et al.*, this *Journal*, 1960, **37**, 753), stipulated the *p*H range of 2.1 to 2.3 and the exposure period of fifteen hours as the necessary optimum conditions. The present communication deals with the separation of uranium from thorium, zirconium, and manganese by the same method, maintaining the same *p*H range and the period of exposure. The effect of variation of the alcoholic composition on the purity and recovery of the product has been investigated in each case.

EXPERIMENTAL

Uranium nitrate, zirconium nitrate, and manganese sulphate used were of E.Merck quality. Thorium nitrate was of B. D. H. AnalaR quality. The preparation of the solutions for photolysis and the analysis of the products obtained after exposure were carried out as reported previously (Singh *et al.*, *Proc. Ind. Acad. Sci.*, 1959, **50A**, 129).

Table I shows that in case of separation of uranium from thorium, single-stage photolysis yields uranium of 96% purity. When photolysis was carried out for the second time, the purity of uranium recovered went up to 99.8%, as can be seen from Table II. It is evident that 20 to 30% alcoholic composition is suitable for photolysis. When separation is made from zirconium and manganese, single-stage photolysis yields uranium of 99.8% purity, though increase of alcoholic composition has a marked effect so far as recovery of uranium from manganese is concerned. The analytical data for the recovery of uranium from zirconium and manganese have been recorded in Tables III and IV respectively.

TABLE I

Separation of uranium from thorium.

Composition of the mixture as oxides.		%Alcohol.	Analysis of precipitate.		%Purity.	%Recovery.
U_3O_8.	ThO_2.		Total oxide by ignition.	U_3O_8 by Cd reductor.		
417.2 mg.	85.4 mg.	20	376.0 mg.	363.9 mg.	96.8	87.2
417.2	85.4	30	397.5	383.6	96.5	92.0
417.2	85.4	40	404.5	375.8	92.9	90.1
417.2	85.4	50	411.5	317.9	90.4	89.1

TABLE II

Composition of the mixture as oxides.		Percentage of alcohol.		Analysis of perecipitate.		%Purity.	%Recovery.
U_3O_8.	ThO_2.	1st phtolysis.	2nd photo-lysis.	Total oxide by ignition	U_3O_8 by Cd. reductor.		
417.2 mg.	85.4 mg.	20	20	373.4 mg.	372.7 mg.	99.8	89.3
417.2	85.4	20	50	375.3	372.2	99.1	89.2

TABLE III

Separation of uranium from zirconium.

Composition of the mixture as oxides.		%Alcohol.	Analysis of precipitate.		%Purity.	%Recovery.
U_3O_8.	ZrO_2.		Total oxide by ignition.	U_3O_8 by Cd reductor.		
417.2 mg.	110.3 mg.	20	370.3 mg.	369.2 mg.	99.7	88.5
417.2	110.3	30	384.6	383.8	99.8	92.0
417.2	110.3	40	395.6	394.8	99.8	94.5
417.2	110.3	50	397.4	396.7	99.8	95.1

TABLE IV

Separation of uranium from manganese.

Composition of the mixture as oxides.		%Alcohol.	Analysis of precipitate.		%Purity.	%Recovery.
U_3O_8.	MnO_2.		Total oxide by ignition.	U_3O_8 by Cd reductor.		
417.2 mg.	103.9 mg.	20	293.9 mg.	293.3 mg.	99.8	70.3
417.2	103.9	30	315.1	314.6	99.8	75.4
417.2	103.9	40	370.2	369.2	99.7	88.5
417.2	103.9	50	373.0	371.9	99.7	89.1

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Spectrophotometric and Potentiometric Studies on Nickel Thiocyanate Complex

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The rection between Ni^{2+} and CNS^- has been studied by spectrophotometric and potentiometric methods. The thermodynamic dissociation constant of the species $NiCNS^+$ has been determined at 25° by spectrophotometric method and at 35° by the potentiometric method using a concentration cell of the type:

Ag, AgCNS | CNS^- (C_1) || salt bridge || CNS^- (C_1), Ni^{2+} (C_2) | AgCNS, Ag.

From the experimental data,— ΔF, ΔH and ΔS for the formation of $NiCNS^+$ have been calculated which are 2048 cal. $mole^{-1}$,-13.17 K cal. and 51.1 cal. $mole^{-1}$ deg^{-1} respectively at 25°.

Thiocyanate ion (CNS^-) is known to form complexes with various bivalent and trivalent metal ions. Franaeus (*Acta Chem. Scand.*, 1953, **7**, 21) studied nickel-thiocyanate system by extinctiometric method at 20°. The complexity constants for the species $NiCNS^+$ and $Ni(CNS)_2$ were determined at sodium perchlorate concentration of 1.0*M*. In the present work the above system has been studied thoroughly by spectrophotometric as well as the potentiometric method. The dissociation constant of the $NiCNS^+$ species has been calculated at zero ionic strength with an idea to get the thermodynamic dissociation constant.

EXPERIMENTAL

Nickel perchlorate was prepared by adding an excess of nickel carbonate (E. Merck, G. R.) to dilute perchloric acid (E. Merck, G.R.). The solution was filtered and the nickel content was estimated by the dimethylglyoxime method.

B.D.H. 'AnalaR' sample of potassium thiocyanate was used as the ligand. It was estimated by Volhard's method (Vogel, 'Text-book of Quantitative Inorganic Analysis'', 2nd. ed., p. 256). All other chemicals used were of the reagent grade. The solutions were prepared in double-distilled water.

For absorption measurements Hilger-Watt's 'UVISPEK' spectrophotometer, model H 700-303, was used. The solutions were taken in quartz cells of 3 cm length. The readings were taken with cells interchanged as in our earlier work (Das and Aditya, this *Journal*, 1959, **36**, 473). The optical measurements were taken at the room temperature which varied between 24° and 26° during the course of measurements.

For determination of stability constant of the complex, the absorbancies of solutions containing a fixed amount of nickel with varying concentrations of potassium thiocyanate were taken at wave lengths 660, 690, and 720 mμ. The concentration ranges of potassium thiocyanate were chosen with care such that the concentration of potassium perchlorate formed by the interaction of the reactants did not exceed its solubility limit.

In the potentiometric work, a Tinsley Vernier potentiometer was used for the E.M.F. measurements. The Ag, AgCNS | CNS^- electrode was prepared by the method suggested by Parida, Aditya, and Prasad (*ibid.*, 1952, **29,** 377), improved upon by Vanderzee and Smith (*J. Amer. Chem. Soc.*, 1956, **78,** 721). For the potentiometric measurements concentration cells of the type,

$$Ag,\ AgCNS \mid CNS^-(C_1) \parallel \text{salt bridge} \parallel CNS^-(C_1),\ Ni^{2+}(C_2) \mid Ag\text{-}\ CNS,\ Ag,$$

were set up. The salt bridge was of the type used by Nath, Aditya and Prasad (this *Journal*, 1951, **28,** 683). A saturated ammonium nitrate solution was used in the bridge. The arrangements were set up inside an air thermostat at 35°. Experiments were done in duplicate and the readings agreed within $\pm$ 0.2 mv.

TABLE I

Cell = 3 cm. Temp.=25°.

Conc. of Ni^{2+} (g. mole/litre).	Conc. of CNS^- (g. mole/litre).	Optical density. 660 mμ.	690 mμ.	720 mμ.
0.06	0.05	0.475	0.456	0.502
0.06	0.06	0.476	0.467	0.508
0.06	0.07	0.496	0.476	0.512
0.06	0.09	0.515	0.500	0.530
0.06	0.10	0.531	0.515	0.542
0.06	0.12	0.545	0.527	0.550
0.06	0.14	0.570	0.540	0.570
0.06	0.15	0.576	0.547	0.577

K_d (from the data at 660 mμ) = 0.0338.
K_d (from the data at 690 mμ) = 0.0323. Average K_d=0.0315.
K_d (from data at 720 mμ) = 0.0286

TABLE II

Temperature = 35°.

Conc. of Ni^{2+} (g. mole/litre).	Conc. of CNS^- (g. mole/litre).	Mean E.M.F. (volts)	Ionic strength.	$K_d \times 10^2$.
0.10	0.10	0.02115	0.300	1.207
0.04	0.10	0.00915	0.168	0.247
0.07	0.08	0.01651	0.223	1.417
0.06	0.08	0.01450	0.200	1.433
0.05	0.08	0.01124	0.182	1.822
0.04	0.06	0.01124	0.144	1.672
0.04	0.08	0.01034	0.155	1.382
0.03	0.06	0.00901	0.120	1.563
0.03	0.03	0.01225	0.102	1.669
0.04	0.04	0.01301	0.134	1.826

Average K_d=1.524 ($\pm$0.045)$\times 10^{-2}$.

DISCUSSION

Spectrophotometric Method

The effect of addition of potassium thiocyanate on the absorption spectrum of nickel perchlorate in the visible was studied. Nickel perchlorate has an absorption

maximum at 730 mμ. The addition of CNS^- ion changes the absorbancy of the solution considerably although no appreciable change in the absorption maximum is observed. The change in absorbancy indicates reaction between Ni^{2+} and CNS^- ions. From the absorbancies of solutions containing nickel and thiocyanate ions, the stability constant has been calculated in the following manner.

The equilibrium between Ni^{2+} and CNS^- ions may be represented as

$$Ni^{2+} + CNS^- \rightleftharpoons NiCNS^+$$
$$NiCNS^+ + CNS^- \rightleftharpoons Ni(CNS)_2$$

and higher complexes. For the present calculation only $NiCNS^+$ species has been considered. The assumption is based on the fact that nickel halides are highly dissociated in solution. In the work on nickel acetate from this laboratory (this *Journal*, 1953, **30**, 735) it has been shown that (in case of $NiAc_2$ in solution) the stage $NiAc_2 \rightarrow NiAc^+ + Ac^-$, is practically complete. Therefore, for the present, let us consider the equilibrium,

$$\underset{(C_1-x)}{Ni^{2+}} + \underset{(C_2-x)}{CNS^-} \rightleftharpoons \underset{x}{NiCNS^+}$$

Let C_1 and C_2 be the original concentrations of nickel perchlorate and potassium thiocyanate respectively and 'x', the concentration of $NiCNS^+$ formed, 'd_1', the absorbancy of the solution with no thiocyanate in it, 'd_2', the absorbancy of a solution containing thiocyanate, and b_1 and b_2, the extinction coefficient of the Ni^{2+} and $NiCNS^+$ species respectively. Then we have,

$$d_1 = \epsilon_1 C_1 l \quad .. \quad .. \quad .. \quad (1)$$
$$d_2 = \epsilon_2 x l + \epsilon_1 (C_1 - x) l \quad .. \quad .. \quad (2)$$

Combining equations 1 and 2, we get

$$x = \frac{d_2 - d_1}{(\epsilon_2 - \epsilon_1) l} \quad .. \quad .. \quad (3)$$

Substituting the expression (3) in the stability constant (K) expression, we have

$$K = \frac{x}{(C_1-x)(C_2-x)} \times \frac{f_{NiCNS^+}}{f_{CNS^-} - f_{Ni^{2+}}}$$

$$= \frac{x}{(C_1-x)(C_2-x)} \times \frac{1}{f_{Ni^{2+}}},$$

$$\frac{C_1}{d_2-d_1} = \frac{1}{(\epsilon_2-\epsilon_1)l} + \frac{1}{K(\epsilon_2-\epsilon_1)\, l\, (C_2-x).\, f_{Ni^{2+}}}.$$

According to the above equation, the slope and the intercept of the straight line on plotting $C_1/(d_2-d_1)$ against $1/(C_2-x)$. $f_{Ni^{2+}}$ will give the value of the stability constant. Since f and x are not known, a series of approximation is done before the above equation can be utilised for obtaining a value of the association constant.

As first approximation x is taken to be equal to zero and $f_{Ni^{2+}}$ as unity, $C_1/(d_2-d_1)$ is plotted against $1/C_2$. From the intercept, an approximate value of $(\epsilon_2-\epsilon_1)$ and ϵ_2 can be obtained, ϵ_1 being known from direct determinations. Having known ϵ_2, the value of x can be calculated by using equation (3). This approximate concentration of the complex

will give an approximate value of the free reactants. From these approximate values, the ionic strength of the solution and hence an approximate activity coefficient $f_{Ni^{2+}}$ can be calculated. Now $C_1/(d_2-d_1)$ is plotted against $1/(C_2-x)\, f'_{Ni^{2+}}$ to obtain a better value of ϵ_2 and hence the concentration of the complex. The ionic strength is calculated again and a better plot obtained. The process is repeated till constant values of the intercept and the slope are obtained. Incidentally, in the first rough plots, the points lie scattered and a mean straight line is drawn, but with two or at best three approximations, the points lie fairly well on a straight line. This further justifies our assumption regarding only one complex species.

Because of the lack of knowledge of the ionic radius, the Debye-Hückel equation could not be used in calculating the activity coefficient of ions. Instead, an alternative empirical relationship suggested by Davies (*J. Chem. Soc.*, 1938, 2093),

$$-\log f_i = 0.5\ Z_i^2 \left\{ \frac{\mu^{\frac{1}{2}}}{(1+\mu^{\frac{1}{2}})} - C\mu \right\}$$

where $C = 0.2$ and Z_i, the valency of the ion and μ, the ionic strength, have been used. The results are recorded in Table I. The average value of the dissociation constant of $NiCNS^+$ at $25^\circ \pm 1^\circ$ is 3.15×10^{-2}.

Potentiometric Method

Coming to the potentiometric measurements, the E. M. F. of the cell:

$$\text{Ag, AgCNS} \mid \text{KCNS}\ (C_1) \parallel \begin{matrix}\text{saturated} \\ NH_4NO_3\ \text{bridge}\end{matrix} \parallel \begin{matrix}\text{KCNS}(C_1) \\ Ni(ClO_4)_2\ (C_2)\end{matrix} \mid \text{AgCNS, Ag}$$

is given by the expression,

$$E = RT/F\ \ln \frac{a_1}{a_2},$$

where a_2 is the activity of the thiocyanate ion in the solution containing both potassium thiocyanate and nickel perchlorate solutions and a_1, the activity in the solution containing no nickel ions, assuming that the liquid junction potential is negligible (practically eliminated by the use of the salt bridge). From the above expression, the activity of the CNS^- ion in solution can be calculated. The ionic strength of the solution was calculated by the method of approximation. As a first approximation, the concentration of the $NiCNS^+$ species is taken to be zero and the ionic strength of the solution estimated. Using the activity coefficient of thiocyanate ion at this ionic strength, the concentration of the free CNS^- ions is calculated. A knowledge of the free thiocyanate gives the concentration of $NiCNS^+$ formed and the free nickel ion in solution. With these more accurate estimation of the ionic strength is made. The process is repeated till a constant value is obtained for the ionic strength of the solution. The activity coefficients of the ions have been calculated on the basis of the equation, already mentioned, as was used in the calculation by using the spectrophotometric data. Thus having calculated the concentrations of the complex species, the association constant is evaluated. The results are recorded in Table II. The average value of the dissociation constant of $NiCNS^+$ complex, found by the potentiometric method, is 1.525×10^{-2} at 35°.

The potentiometric measurements have been made at 35° and the spectrophotometric ones at 25°. Although in the present investigation, we have not seen how the measurements by the two methods at the same temperature compare with each other, the agreement by the two methods is reported to be good. Franaeus (*Acta Chem. Scand.*, 1951, **5**, 139) studied the complex formed between Cu^{2+} and NO_2^- ions at 20°, using spectrophotometric as well as potentiometric methods. The former method gave a value of 1.30 and the latter 1.23 for the logarithm of the formation constant. A similar agreement has been observed in the case of Fe^{3+}—CNS^- complex (Betts and Dainton, *J. Amer. Chem. Soc.*, 1953, **75**, 5721; spectrophotometric method, log K_1=2.94; Lawrance, *Trans. Faraday Soc.*, 1956, **52**, 236; potentiometric method, log K_1 =3.03). So from our results at 35° and 25°, we have calculated the constant at 20° because we thought it might be interesting to compare our results with that of Franaeus, who determined the equilibrium constant from the same complex at 20°. Our value comes out to be 0.0456 at 20° and zero ionic strength, whereas Franaeus's value is 0.0666 at the same temperature but at an ionic strength of 1 *M*. It is not possible to assess the quantitative effect of this difference in ionic strength. Nevertheless, since the increase in ionic strength is likely to increase the dissociation constant, this difference is qualitatively justified.

From our results, the standard free energy change ($-\triangle F$) for the reaction

$$Ni^{2+} + CNS^- \rightleftharpoons NiCNS^+,$$

comes out to be 2.048×10^3 cal. $mole^{-1}$ at 25° and 2.563×10^3 cal. $mole^{-1}$ at 35°. The value of $-\triangle H$, for the formtion of $NiCNS^+$, is −13.17 Kcal. $mole^{-1}$ and $\triangle S$, for the formation at 25° is 51.1 cal. $mole^{-1}$. $deg.^{-1}$.

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Reactive Methylene Compounds. Part XI. Condensation of Benzeneazo-β-diketones with Phenylhydrazine

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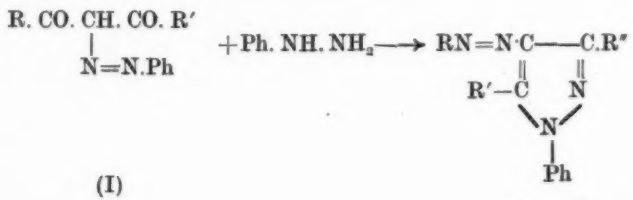
Several 1-phenyl-3,5-dimethyl-, 1,5-diphenyl-3-methyl-, and 1,3,5-triphenyl-4-benzeneazopyrazoles have been synthesised and their characteristics are described.

Interest in the chemotherapeutic activity of certain pyrazole derivatives has led to the synthesis of some of them by the condensations of 1,3-dicarbonyl compounds with phenylhydrazines (Garg, *J. Org. Chem.*, 1961, **26**, 948). In the present communication the behaviour of benzeneazo derivatives of acetylacetone, benzoylacetone, and dibenzoylmethane with phenylhydrazine has been investigated.



(I) (II : R=Ph).

I a: R=R′=Me.
I b: R=R′=Ph.
I c: R=Me; R′=Ph.

4-Benzeneazopyrazoles (II) have been found to be formed; intermediate dihydrazones could not be isolated (cf. Beyer and Claisen, *Ber.*, 1888, **21**, 1697).

Substituted benzeneazopyrazoles are highly coloured substance, varying in colour from yellow to red. These are soluble in acetic acid, ethanol, etc.

EXPERIMENTAL**

The synthesis of benzeneazo derivatives were effected by the action of benzenediazonium salts on β-diketones (Garg, this *Journal*, 1960, **37**, 626).

1-Phenyl-3, 5-dimethyl-4-benzeneazopyrazole.—A solution of benzeneazoacetylacetone (0.01*M*) in ethanol (15 c.c.) and phenylhydrazine (0.01*M*) in glacial acetic acid were heated on a water bath for 4 hours. On cooling and dilution with water, a precipitate separated which on recrystallisation from ethanol gave 1-phenyl-3,5-dimethyl-4-benzeneazopyrazole.

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**Melting points are uncorrected.

Characteristics of different 1-phenyl-3,5-dimethyl-4-benzeneazopyrazoles are shown in Table I.

TABLE I

1-Phenyl-3-5-dimethyl-4-benzeneazopyrazoles.

No.	R*.	Yield.	M.P.	Colour.	Formula.	Found.	Calc.
1.	Phenyl	78%	62°	Orange	$C_{17}H_{16}N_4$	N : 19.94	20.28
2.	4-Methoxyphenyl	72	85°	Pale yellow	$C_{18}H_{18}ON_4$	N : 18.08	18.30
3.	4-Bromophenyl	79	136°	Light yellow	$C_{17}H_{15}N_4Br$	Br: 22.24	22.53
4.	4-Chlorophenyl	79	109°	Yellow	$C_{17}H_{15}N_4Cl$	Cl : 11.11	11.43
5.	3-Chlorophenyl	73	56°	Light yellow	$C_{17}H_{15}N_4Cl$	Cl : 11.08	11.43
6.	2-Chlorophenyl	71	107°	Orange-red	$C_{17}H_{15}N_4Cl$	Cl : 11.18	11.43
7.	4-Nitrophenyl	81	140°	Orange-yellow	$C_{17}H_{15}O_2N_5$	N : 21.62	21.80
8.	3-Nitrophenyl	80	112°	Brownish red	$C_{17}H_{15}O_2N_5$	N : 21.56	21.80
9.	2-Nitro-4-chlorophenyl	80	122°	Orange	$C_{17}H_{14}O_2N_5Cl$	Cl: 9.58	9.98

*Vide structure (II: R′=R″=Me).

1,5-*Diphenyl-3-methyl-4-benzeneazopyrazole* was prepared from bezeneazobenzoylacetone and isolated in the same manner as above. Characteristics of different 1,5-diphenyl-3-methyl-4-benzeneazopyrazoles are recorded in Table II.

TABLE II

1, 5-Diphenyl-3-methyl-4-benzeneazopyrazoles.

No.	R*.	Yield.	M.P.	Colour.	Formula.	Found.	Calc.
1.	Phenyl	80%	136°	Golden yellow	$C_{22}H_{18}N_4$	N : 16.32	16.56
2.	4-Methoxyphenyl	74	104°	Yellow	$C_{23}H_{20}ON_4$	N : 15.04	15.21
3.	4-Bromophenyl	82	106°	Orange-yellow	$C_{22}H_{17}N_4Br$	Br: 18.82	19.18
4.	4-Chlorophenyl	81	120°	Pale yellow	$C_{22}H_{17}N_4Cl$	Cl : 9.14	9.53
5.	3-Chlorophenyl	80	96°	Golden yellow	$C_{22}H_{17}N_4Cl$	Cl : 9.21	9.53
6.	2-Chlorophenyl	80	122°	Orange-red	$C_{22}H_{17}N_4Cl$	Cl : 9.11	9.53
7.	4-Methylphenyl	68	117°	Orange	$C_{23}H_{20}N_4$	N : 15.61	15.90
8.	3-Methylphenyl	62	84°	,,	$C_{23}H_{20}N_4$	N : 15.56	15.90
9.	2-Nitro-4-chlorophenyl	81	162°	,,	$C_{22}H_{16}O_2N_5Cl$	Cl : 8.21	8.50

*Vide structure (II: R′=Ph; R″=Me).

1, 3, 5-*Triphenyl-4-benzeneazopyrazole*.—A solution of benzeneazodibenzoylmethane (0.01*M*) in glacial acetic acid (15 c.c.) and phenylhydrazine (0.01*M*) were heated on a water bath for 3 hours. On dilution, a crystalline precipitate was obtained, which was recrystallised from acetic acid. Characteristics of different 1,3,5-triphenyl-4-benzeneazopyrazoles are described in Table III.

TABLE III

Characteristics of 1,3,5-triphenyl-4-benzeneazopyrazoles.

No.	R*.	Yield.	M.P.	Colour.	Formula.	Found.	Calc.
1.	Phenyl	80%	156°	Orange-red	$C_{27}H_{20}N_4$	N : 13.81	14.00
2.	4-Methoxyphenyl	74	136°	Orange-yellow	$C_{28}H_{22}ON_4$	N : 12.84	13.02
3.	4-Bromophenyl	82	162°	Orange-yellow	$C_{27}H_{19}N_4Br$	Br : 16.34	16.70
4.	4-Chlorophenyl	81	152°	Orange-red	$C_{27}H_{19}N_4Cl$	Cl : 8.01	8.16
5.	3-Chlorophenyl	80	122°	Orange-yellow	$C_{27}H_{19}N_4Cl$	Cl : 7.82	8.16
6.	2-Chlorophenyl	80	125°	Orange-red	$C_{27}H_{19}N_4Cl$	Cl : 7.84	8.16
7.	4-Nitrophenyl	84	147°	Orange-red	$C_{27}H_{19}O_2N_5$	N : 15.61	15.73
8.	3-Nitrophenyl	81	140°	Orange	$C_{27}H_{19}O_2N_5$	N : 15.52	15.73
9.	2-Nitro-4-chlorophenyl	83	104°	Dull red	$C_{27}H_{18}O_2N_5Cl$	Cl : 7.12	7.40

*Vide structure (II: R′=R″=Ph).

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Synthesis of Imidazoles. Part I. Preparation of some 4(or 5)-Substituted Imidazoles

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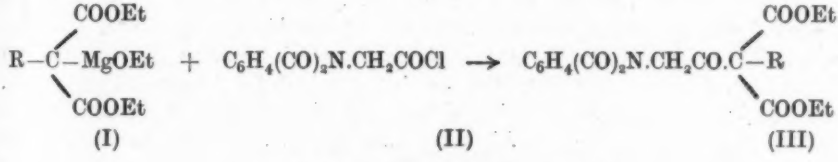
As the condensation of ethyl 3-phthalimidoacetoacetate with alkyl (or aryl) halides fails to yield ethyl 1-alkyl (or aryl)-3-phthalimidoacetoacetates, the desired products have been prepared in satisfactory yields by condensing ethoxymagnesium salt of substituted diethyl malonate and phthalimidoacetyl chloride. The substituted acetoacetates have been hydrolised (dil.HCl) and the corresponding aminoketones treated with potassium sulphocyanide to yield 2-mercapto-4(or 5)-alkyl (or aryl)-imidazoles. The latter have been oxidised to the corresponding imidazoles.

Imidazoles and mercaptoimidazoles (Gabriel, *Ber.*, 1893, **26**, 2197) are well known for their biological activities; with this end in view some of these compounds have been prepared by us employing a more convenient method for the preparation of ∝-aminoketones.

The desired ∝-aminoketones have been prepared by ketonic hydrolysis of ethyl 1-alkyl(or aryl)-3-phthalimidoacetoacetate(IV). For the preparation of the latter, the sodium salt of ethyl 3-phthalimdoacetoacetate (this *Journal*, 1961, **38**, 785) was condensed with suitable alkyl halides. This, however resulted in the formation of a deep red-coloured semisolid from which the desired compounds could not be crystallised. Hence an alternative procedure, similar to that employed for the preparation of ethyl 3-phthalimidoacetoacetate (*loc. cit.*), was employed. Ethoxymagnesium salts of substituted diethyl malonates (I) were condensed with phthalimidoacetyl chloride (II) in dry ether to afford ethyl 1-substituted-3-phthalimidoacetoacetate (IV) in satisfactory yields.



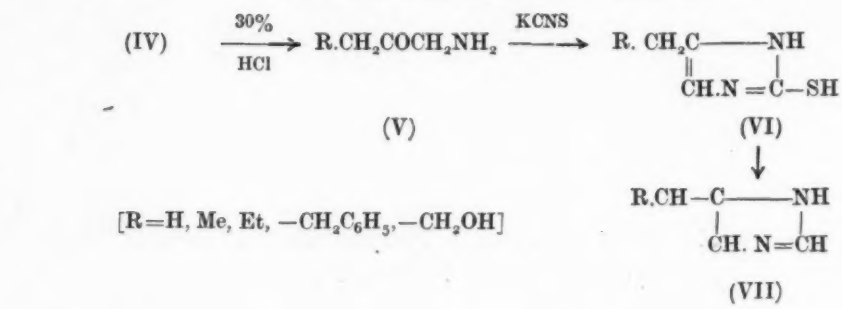
(I) (II) (III)

$C_6H_4(CO)_2N.CH_2CO.CH(R).COOEt$

(IV)

[R=Me, Et, $-CH_2C_6H_5$, $-CH_2OC_2H_5$]

Ethyl 1-alkyl (or aryl)-3-phthalimidoacetoacetates (IV) were then hydrolysed by 30% HCl. The hydrochlorides of ∝-aminoketones (V) on heating with an aqueous solution of KCNS afforded the mercaptoimidazoles (VI), which were purified through the mercury salts. These were then oxidised by HNO_3 (dil.), $FeCl_3$, etc., when the corresponding imidazoles (VII) were regenerated.



EXPERIMENTAL

Attempted Method for the Preparation of Ethyl 1-*Alkyl* (*or aryl*) -3-*phthalimidoacetoacetate*.—Na(1.5g., 0.05 g. atom) was dissolved in dry ethanol(50 c.c.) in a 500 c.c. three-necked flask and to it a solution of ethyl 3-phthalimidoacetoacetate (13.7g., 0.05*M*) in dry ethanol (200 c.c.) was added during 15 minutes with brisk stirring. After 60 minutes of further stirring redistilled alkyl (or aryl) halide (0.05 *M*) was added dropwise during 30 minutes and the mixtu re was left overnight. It was refluxed on a water bath for 2 hours.

The reaction proceeded smoothly till nearly 2/3 solid had disappeared, when the reaction m ixture assumed red colour which gradually turned intense red. After removing the solvent under diminished pressure, the residue was dissolved in benzene and extracted with two 10 c.c. portions of HCl (cold, dilute). The organic layer was washed with water and the solvent removed. A red semisolid mass, thus obtained, could not be crystallised. The reaction was repeated in benzene and ether solutions with the same result.

Ethyl 1-*Methyl*-3-*phthalimidoacetoacetate*.—In a 500 c.c. three-necked flask were placed Mg turnings (2.4 g., 0.1g. atom), dry ethanol (15 c.c.) and dry CCl_4 (0.5 c.c.). From the dropping funnel a mixture of diethyl methylmalonate (17.5g., 0.1*M*) and dry ethanol (20 c.c.) was slowly added at such a rate that a vigorous reaction was maintained. When the reaction had subsided, sodium-dried ether (30 c.c.) was added and the mixture was gently refluxed till magnesium disappeared. The solvent was then removed under diminished pressure. The residual syrup was dissolved in sodium-dried benzene (25 c.c.) and the solvent removed. The flask was then heated on a water bath for 2 hours under suction. After cooling, the syrup was dissolved in sodium-dried ether (60 c.c.). A solution of pure phthalimidoacetyl chloride (24 g., 0.1*M*) in dry ether (100 c.c.) was then added at such a rate that a vigorous reaction was maintained. The reaction mixture was gently refluxed for 1½ hours, cooled in an ice bath, and quickly filtered through cotton wool. The filtrate was washed successively with 10 c.c. portions of water (thrice), dilute H_2SO_4, and water. The organic layer was denuded of the solvent and the residue steam distilled till a clear filtrate was obtained. The contents of the distillation flask were cooled and filtered. The crystalline precipitate was dissolved in benzene and filtered again. From this filtrate benzene was removed completely under reduced pressure. The residue was dissolved in hot ethanol and on cooling, the solution yielded the desired compound, which was twice recrystallised from ethanol, m.p. 61°, yield 57%. (Found: C, 61.74; H, 4.51; N, 4.4. $C_{15}H_{15}O_5N$ requires C, 6 .28; H, 5.18; N, 4.8%).

Ethyl 1-methyl-3-phthalimidoacetoacetate is soluble in hot ethanol, glacial acetic acid, ether, and benzene and gives a red colour with ferric chloride. *Semicarbazone*, m.p. 57°. (Found: N, 16.2. $C_{16}H_{18}O_5N_4$ requires N, 16.19%).

Ethyl 1-*ethyl*-3-*phthalimidoacetoacetate* was prepared by a method similar to that described above, using Mg (2.4 g.), ethyl diethylmalonate (19 g.) and phthalimidoacetyl chloride (22.4 g.). It was twice recrystallised from ethanol, m.p. 70°, yield 54%. (Found: C, 62.79; H, 5.78; N, 4.62. $C_{16}H_{17}O_5N$ requires C, 63.3; H, 5.6; N, 4.41%).

The solubility of the ester and its colour reaction with ferric chloride are the same as of the preceding ester. *Samicarbazone*, m.p 65°. (Found: N, 15.83. $C_{17}H_{20}O_5N_4$ requires N, 15.56%). *Pyrazolone*, m.p. 63°. (Found: N, 12.49. $C_{20}H_{17}O_3N_3$ requires N, 12.1%).

Ethyl 1-*benzyl*-3-*phthalimidoacetoacetate* was prepared as usual, using Mg (2.4 g.), diethyl benzylmalonate (25 g.), and phthalimidoacetyl chloride (22.4 g.). It was thrice crystallised from ethanol, m.p. 98°, yield 38.6%. (Found: C, 68.77; H, 5.01; N, 3.56. $C_{21}H_{19}O_5N$ requires C, 69.04; H, 5.2; N, 3.83%. The solubility of the ester and its colour with $FeCl_3$ are same as with the preceding esters. *Semicarbazone*, m.p. 104°. (Found: N, 13.21. $C_{22}H_{22}O_5N_4$ requires N, 13.27%). *Pyralazone*, m.p. 103°. (Found: N, 10.61. $C_{25}H_{19}O_5N_3$ requires N, 10.27%).

Ethyl 1-*ethoxymethyl*-3-*phthalimidoacetoacetate* was prepared in 57% yield by following the procedure adopted as above with diethyl ethoxymethylmalonate (22.4 g.) using the same molar proportion of the other constituents. After twice crystallisation from ethanol it melted at 108°. (Found: C, 61.74; H, 5.43; N, 4.04. $C_{17}H_{19}O_6N$ requires C, 61.26; H, 5.70; N, 4.20%).

The ester is freely soluble in ethanol, glacial acetic acid, ether, and benzene. It develops a red colour with ferric chloride. *Semicarbazone*, m.p. 112°. (Found: N, 14.52. $C_{18}H_{22}O_6N_4$ requires N, 14.36%.) *Pyralazone*, m.p. 115°. (Found: N, 11.41. $C_{21}H_{19}O_4N_3$ requires N, 11.14%).

4(*or* 5)-*Methylimidazole*.—Ethyl 3-phthalimidoacetoacetate (27.5 g.) was heated with 30% HCl (200 c.c.) for 3 hours till the ester had dissolved. On cooling most of the phthalic acid separated. This was filtered, the filtrate concentrated to half the volume on a water bath, and then chilled in ice. Precipitated phthalic acid was again filtered and the filtrate evaporated to dryness under reduced pressure. Highly hygroscopic *hydrochloride of the aminoketone*, m.p. 75° (H_2PtCl_6, m.p. 189°), thus obtained, was dissolved in ethanol and precipitated with ether. The precipitate was quickly filtered and dissolved in water (10 c.c.). KCNS (8 g.), dissolved in water (8 c.c.), was then added and the mixture heated on a water bath for 2 hours. It was slowly evaporated to dryness. The residue was dissolved in warm water (100 c.c.) and treated with a saturated solution of mercuric acetate till the precipitation was complete. The light yellow precipitate of mercury complex of 2-*mercapto*-4(or 5)-*methylimidazole* was suspended in water (50 c.c.), made acidic with HCl (dil.), and H_2S gas passed. Mercury sulphide was filtered and washed twice with 20 c.c. portions of water. The combined filtrate and washings were treated with charcoal and filtered. The clear filtrate was evaporated to dryness when hydrochloride of 2-mercapto-4(or 5)-methylimidazole was obtained as a yellowish white, hygroscopic substance. This was dissolved in dry ethanol and neutralised with EtOH—KOH. Precipita-

ted KCl was filtered and the filtrate evaporated to crystallisation, m.p.246°(lit. m.p.245-46°), yield 3.42 g. (Found: N, 24.22; S, 28.30. Calc. for $C_4H_6N_2S$: N, 24.5; S, 28.02%). This gives 2-*acetoxymercapto*-4(or 5)-*methylimidazole*, m.p. 200°. (Found: N, 15.98; S, 18.67. Calc. for $C_6H_8O_2N_2S$: N, 16.28; S, 18.60%).

2-*Mercapto*-4(*or* 5)-*methylimdazole* was oxidised by warming slowly with 30% HNO_3. The light red solution slowly changed to yellow. The solution was evaporated to dryness at minimal pressure and the residue was taken in dry ethanol. This was then neutralised with EtOH-KOH and filtered. From the filtrate the solvent was removed under diminished pressure. The residue after crystallisation from ethanol-ether gave 4(or 5)-methylimidazole, m.p. 56° (lit. m.p. 56°). (Found: C, 58.69; H, 7.42; N, 34.36. Calc. for $C_4H_6N_2$: C, 58.54; H, 7.32; N, 34.15%). *Hydrochloride*, m.p. 119°; *picrate*, m.p. 164°.

4(*or* 5)-*Ethylimidazole*.—Ethyl 1-methyl-3-phthalimidoacetoacetate (14.45 g.) was hydrolysed by 30% HCl when hydrochloride of aminomethylketone, m.p. 151° (H_2PtCl_6, m.p.171°), was obtained; by following the procedure described above, but using 6g. of KCNS, 1.6 g. of a cream coloured 2-*mercapto*-4(*or* 5)-*ethylimidazole*, which started melting at 210° and decomposed at 260°, was obtained. (Found: N, 21.66; S, 25.29. $C_5H_8N_2S$ requires N, 21.87; S, 25.0%).

2-Mercapto-4(or 5)-ethylimidazole was oxidised by boiling with an aqueous solution of ferric chloride (14 g.) for 12 hours. After leaving overnight, the solution was made alkaline to litmus with 50% K_2CO_3 and filtered. The filtrate was extracted 10-12 times with 50 c.c. portions of $CHCl_3$. The combined extract was dried over anhydrous sodium sulphate. The solvent was again removed. The residue was recrystallised several times with ethanol-ether when 4(*or* 5)-*ethylimidazole*, m.p. 76.5°, was obtained in quantitative yield. (Found: C, 62.19; H, 8.38; N, 29.53. $C_5H_8N_2$ requires C, 62.5; H, 8.33; N, 29.17%). *Nitrate*, m.p 82°; *picrate*, m.p 116°.

4(*or* 5)-*Propyl*^{n}*imidazole*.—Ethyl 1-ethyl-3-phthalimidoacetate (15.2 g.) was hydrolysed similarly and by using 6 g. of KCNS to 2-mercapto-4(or 5)-propyl^{n}imidazole; m.p. 184°, yield 1.3 g. (Found: N, 19.63; S, 22.36. $C_6H_{10}N_2S$ requires N, 19.72; S, 22.54%).

2-Mercapto- 4(or 5)-propyl^{n}imidazole was oxidised by ferric chloride (14 g.) when 4(*or* 5)-*propyl*^{n}*imidazole*, m.p. 66.7°, was obtained in quantitative yield. (Found: C, 65.42; H, 9.48; N, 25.36. $C_6H_{10}N_2$ requires C, 65.46; H, 9.09; N, 25.45%). *Hydrochloride*, m.p. 120°; *picrate*, m.p. 179°.

4(*or* 5)-(*β*-*Phenylethyl*)-*imidazole*.—Ethyl 1-benzyl-3-phthalimidoacetoacetate (18.5 g.) was hydrolysed and treated with KCNS, as described above, when 1.1 g. of 2-*mercapto*-4(*or* 5)-(o-*phenylethylimidazole*, m.p. 260° (decomp.), was obtained. (Found: N, 13.62; S, 16.02. $C_{11}H_{12}N_2S$ requires N, 13.73; S, 15.69%).

2-Mercapto-4(or 5)-(*β*-phenylethyl)-imidazole was oxidised by ferric chloride (14 g.) when 4(or 5)-(*β*-phenylethyl)-imidazole, m.p. 81°, was obtained in quatitative yield. (Found: C, 76.70; H, 7.21; N, 16.52. $C_{11}H_{12}N_2$ requires C, 76.74; H, 6.98; N, 16.28%). *Hydrochloride*, m.p. 146°; *picrate*, m.p. 236° (decomp.).

4(*or* 5)-(*β*-*Hydroxyethyl*)-*imidazole*.—Ethyl 1-ethoxymethyl-3-phthalimidoacetoacetate (16.65 g.) was hydrolysed by HCl (dil.), as described above, and the corresponding

aminoketone was treated with KCNS (6 g.), when 1.3 g. of 2-*mercapto* 4(*or* 5)-(*β-hydroxyethyl-imidazole*, m.p. 193° (lit. m.p. 193°), was obtained. (Found: N, 19.15; S, 22.63. Calc. for $C_5H_8ON_2S$: N, 19.44; S, 22.22%).

2-Mercapto-4(or 5)-(β-hydroxy ethyl)-imidazole was oxidised by ferric chloride (14 g.) when 4(*or* 5)-(*β-hydroxyethyl*)-*imidazole*, m.p. 92°(lit. m.p. 92°), was obtained in quantitative yield. (Found: C, 53.75; H, 6.89; N, 25.43. Calc. for $C_5H_8ON_2$: C, 53.57; H, 7.14; N, 25.0%). The hydrochloride is highly hygroscopic.

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SHORT NOTES

An Equation Linking the Potential of the Stern-Mukherjee Layer with the Electrokinetic Potential ζ

B. N. Ghosh

While the ζ-potential is regarded as the difference of potential between the slipping plane and the interior of the solution, the potential of the Stern-Mukherjee layer (Mukherjee, *Disc. Faraday Soc.*, 1911, **16**, 103; Stern, *Z. Elektrochem.*, 1924, **30**, 508) may be regarded as that between the capillary surface and the slipping plane and should be denoted by $(\psi_o - \zeta)$ where ψ_o is the Nernst or surface potential.

For glass, which behaves as a reversible hydrogen electrode, variation of ψ_o with the concentration C of H^+ ions in solution can be expressed by the equation

$$\psi_o = \frac{kT}{e} \ln \frac{C_o}{C} \qquad .. \qquad (1)$$

where C_o is a constant and k, T, and, e have their usual significance.

Similarly, by applying the Maxwell-Boltzmann law of distribution, one can write

$$C_1 = C \exp. (e\zeta/kT)$$

or

$$\zeta = \frac{kT}{e} \ln \frac{C_1}{C} \qquad .. \qquad (2)$$

where C_1 represents the concentration of H^+ ions at the slipping plane.

Let us denote $(\psi_o - \zeta)/\zeta$ by p. It then follows that,

$$p = \frac{\psi_o - \zeta}{\zeta} = (\ln \frac{C_o}{C} - \ln \frac{C_1}{C}) / \ln \frac{C_1}{C} = \ln \frac{C_o}{C_1} / \ln \frac{C_1}{C}$$

or

$$\ln \frac{C_o}{C_1} = p \ln \frac{C_1}{C} = \ln \frac{C_1^p}{C^p}$$

or

$$C_1 = (C_o C^p)^{1/(p+1)} \qquad .. \qquad (3)$$

Substituting the above value of C_1 in equation (2) and putting $p = 0.8$, we get

$$\zeta = 0.058 \log \left(\frac{C_o}{C}\right)^{1/(1+p)} = 0.032 \log C_o - 0.032 \log C \qquad (4)$$

Rutgers and de Smet (*Trans. Faraday Soc.*, 1945, **51**, 758) have observed that the ζ-potential of Jena glass (16111) capillary wall varies linearly with -log$C$; where C represents the concentration of the H^+ ions in solution in contact with the glass surface and the slope of the line is 0.032 and not 0.058. They have offered an interpretation different from that given above. They also have assumed that the surface potential ϵ (same as-ψ_0 in equation 1) varies according to the equation

$$\epsilon = \frac{RT}{F_n} \ln \frac{C}{C_0}.$$

It has been further assumed by them that (*a*) at C_0 the H^+ ion concentration at the glass wall is not constant, but that it varies with its concentration C in the solution; (*b*) according to the Freundlich adsorption isotherm $C_0 = \propto C^{0.45}$. Finally they have arrived at the equation

$$\epsilon = 0.032 \log C - \epsilon' \qquad .. \qquad (5)$$

where ϵ' is a constant.

It may be pointed out that according to equation (5), it is the surface potential ϵ, and not ζ, which varies linearly with 0.032 log. What has actually been observed is that ζ varies linearly with -log C.

The line of argument, which has been followed by the present author in deriving equation (4), does not involve the assumptions (*a*) and (*b*) and at the same time leads to an expression connecting ζ directly with -log C and p, which has been given a physical significance.

It may be mentioned that by giving suitable values to C_0 and p in equation (4), the results, obtained by Rutgers and de Smet (*loc. cit.*) using other univalent cations between the concentration range of 2×10^2 and $1 \times 10^4 \mu$ equivalents/litre, can also be accounted for fairly satisfactorily.

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Influence of Ionic Strength on the Rate of Alkaline Fading of Brilliant Green

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The effect of neutral salts on the velocity of reactions in solutions has been a subject of study of a number of workers (Long *et al.*, *J. Phys. Coll. Chem.*, 1951, **55**, 813, 829; La Mer, *Chem. Rev.*, 1932, **10**, 179). The study of the above at constant and varied ionic strengths is useful for elucidation of the mechanism of, especially, the charged and uncharged nature of the reacting species involved in the reaction. The mathematical formulation of the salt effects has been developed by Bronsted (*Z. physikal. Chem.*, 1925, **115**, 337), Bjerrum (*ibid.*, 1924, **108**, 82; 1925, **118**, 25), and Christiansen (*ibid.*, 1924, **113**, 35). The present note reports the application of these equations to the kinetic studies of the decomposition of brilliant green (B.G.), viz., 4,4′-bis-diethylaminotriphenylmethyl sulphate, in alkali solution, to carbinol, on which no data exist in the literature.

B. G. of B. D. H. quality was purified according to the methods described elsewhere (Lewis *et al.*, *J. Amer. Chem. Soc.*, 1942, **64**, 1774). KNO_3 used as the neutral salt was a B.D.H. AnalaR reagent. The reaction was followed spectrophotometrically by observing the optical density at various time intervals. Spectrophotometric measurements were carried out using 10 mm corex cells on a Beckman spectrophotometer, model DU, which was provided with a dual thermospacer set for temperature control. All the kinetic studies reported in this communication were carried out at $25^\circ \pm 0.05^\circ$.

Preliminary experiments showed that B.G. was adsorbed at the glass surface (if kept for more than 10 minutes), thus reducing the effective concentration of the dye. This appeared significant because of the low concentration of the substance used. Studies at higher concentrations were not possible on account of the precipitation of carbinol. The reaction was therefore carried out in wax-coated glass vessels; aliquots of the reaction mixtures were drawn out at desired intervals for spectrophotometric estimation of B.G., which showed absorption maximum at 625 mμ, with an extinction coefficient 8.00×10^4 litre $mole^{-1}$ cm^{-1}. The velocity constant of the reaction was obtained by

$$k' = \frac{2.303\ (\triangle \log C_{\text{B.G.}})\ \text{litres}}{(\triangle T)\ (C_{OH^-})\ \text{mole. min.}}$$

The effect of ionic strength (μ) on k' was studied by adding increasing quantities of KNO_3. These data are shown in Fig. 1. It is interesting to note that k' varied markedly with μ. The following equation elucidates the influence of μ on k':

$$\ln k' = \ln k_0' + 2A\ Z_A Z_B \sqrt{\mu} \qquad \ldots \qquad (i)$$

According to eq. (*i*), k' is a linear function of $\sqrt{\mu}$. It is seen from Fig. 1, curve 1, that eq. (*i*) is applicable only for low values of μ. At higher values of μ, the points fall away

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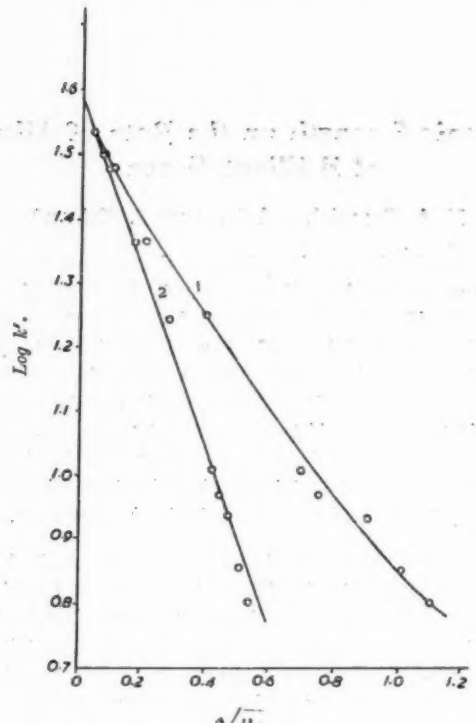

FIG. 1

from the linear plot. This deviation from eq. (*i*) is attributed to the inaccurate values of activity coefficients computed from the Debye-Hückel equation. Applying the modified Debye-Hückel equation for reaction rates (Guntelberg, *Z. physikal. Chem.*, 1926, **123**, 243), we get:

$$\ln k' = \ln k_0' + \frac{2A\ Z_A Z_B \sqrt{\mu}}{1+\sqrt{\mu}} \qquad (ii)$$

which requires a linear plot between k' and $\sqrt{\mu}/(1+\sqrt{\mu})$. Suggestively enough, eq. (*ii*) is valid over a wide range of μ (see Fig. 1, curve 2). The data in Fig. 1 (curve 2) give a value of 38.90 litre mole^{-1} min^{-1} for velocity constant at zero ionic strength (k_0') and a value of—1.2 for $Z_A Z_B$, suggesting thereby that the reaction involves two species with unit charges of opposite sign.

Thanks are due to Prof. S. N. Gundu Rao, Director, National Sugar Institute, for his kind interest and to the Scientific Research Committee, U.P. for a grant to one of them (S. S. K.).

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Reduction of Mercuric Chloride by Oxalic Acid, Induced by Potassium Persulphate

L. K. Saxena and C. P. Singhal

Activation of oxalic acid by oxidising agents, such as $KMnO_4$, $K_2S_2O_8$, etc., exhibited in the ready reduction of mercuric chloride to mercurous state, was first observed by Dhar (*J. Chem. Soc.*, 1917, **111**, 690; this *Journal*, 1928, **5**, 203). The present authors studied the kinetics of the reduction of mercuric chloride by oxalic acid, induced by potassium persulphate (this *Journal*, 1960, **37**, 405), and derived an expression for the rate process on the mechanism suggested. The present note deals with the dependence of period of induction on the concentration of the reactants and the relationship among the amounts of inductor ($K_2S_2O_8$), actor ($H_2C_2O_4$), and acceptor ($HgCl_2$) on the total amount of calomel formed.

Procedure.—The flasks containing the reaction mixture were kept in a thermostat maintained at 60°. After 60 minutes the precipitated mercurous chloride was filtered through a double-walled funnel at ice-water temperature to arrest the reaction. It was then estimated volumetrically by titrating against 0.1*N*-KIO_3 solution (*loc. cit.*). The time between mixing of the reactants and the first appearance of Hg_2Cl_2 precipitate was noted as the period of induction.

Figs. 1 and 2 show the dependence of induction period and the amount of calomel formed (or mercuric chloride reduced) in one hour, respectively, on the concentrations of the reactants at 60°.

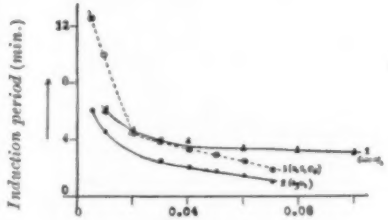

FIG. 1

1. Oxalic acid.
2. $HgCl_2$.
3. $K_2S_2O_8$.

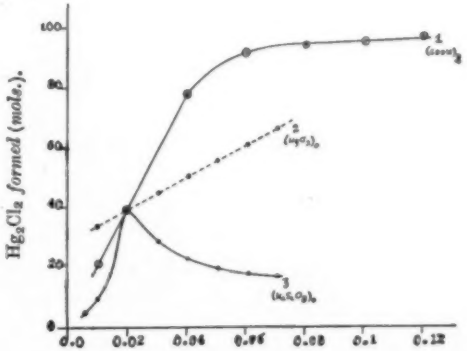

FIG. 2

For curves 1 (both figs.), the initial concentrations of the persulphate and mercuric chloride were kept 0.02*M* each, whereas that of oxalic acid was varied. Similarly for curves

2 and 3, the concentrations of mercuric chloride and persulphate, respectively, were varied while those of the other two reactants were at 0.02 *M* each.

Fig. 1 shows that increase of concentration of any of the reactants decreases the period of indution. Fig. 2, curve 1 shows that the reduction of mercuric chloride increases by increasing the concentration of oxalic acid. It is found to be proportional to the acid concentraction up to 0.04*M* and then slows down. The reduction is proportional to the concentration of mercuric chloride (curve 2). The reduction increases by increasing the concentration of persulphate to 0.02*M* only and then suffers inhibition.

Neither $C_2O_4^{2-}$ nor $S_2O_8^{2-}$ ion alone is able to reduce mercuric chloride, but a mixture of the two does so. This clearly suggests that as a result of interaction of the two ions some active product is produced which reduces Hg^{2+} ion to Hg_2^{2+} state. This active product is possibly the CO_2^- radical, which may be formed during the oxidation of oxalic acid by the persulphate, as has been observed in the oxidation of oxalic acid by potassium permanganate (Weiss, *Trans. Faraday Soc.*, 1947, **53**, 188) and halogens (Griffith and McKeown, *ibid.*, 1932, **28**, 752.)

The role of CO_2^- and SO_4^- radicals as intermediates in the reduction of mercuric chloride has been shown in the mechanism suggested by the authors (*loc. cit.*) and the rate expression derived therefrom explains fully the curves in Fig. 2. The time required for thermal activation of $S_2O_8^{2-}$ ion to break into SO_4^- radical is the induction period and this decreases on increasing the concentration of any of the reactants.

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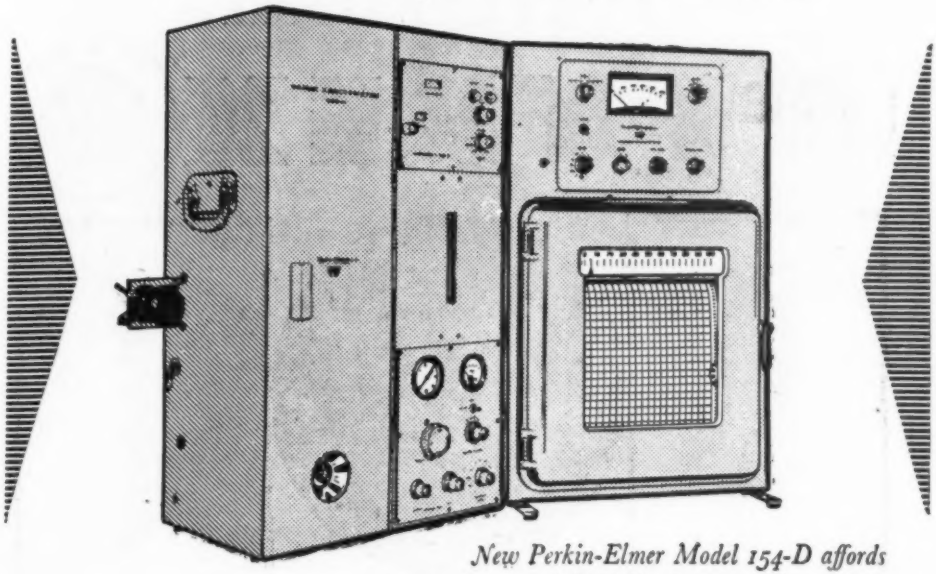

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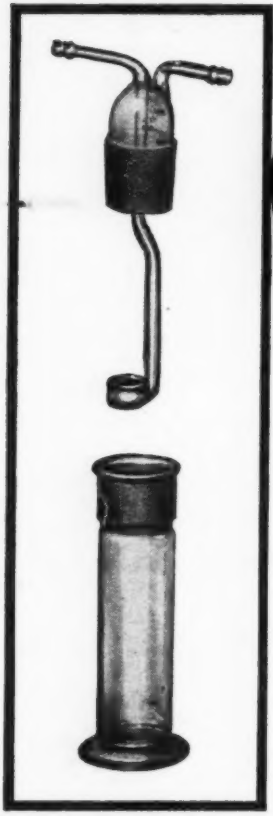

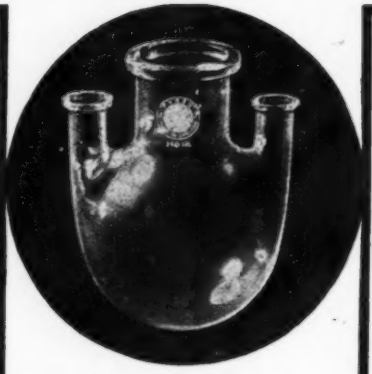

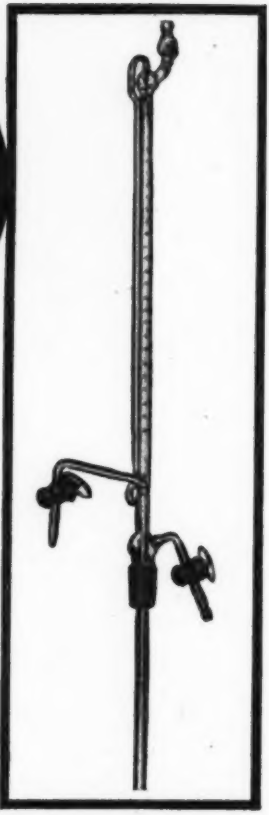

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